

A MULTIPLE-VALUE APPROACH TO DETERMINE THE GROUND AND
SURFACE WATER RELATIONSHIPS IN THE WESTERN SANTA FE RIVER,
COLUMBIA COUNTY, FLORIDA

By

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A MULTIPLE TRACER APPROACH TO DETERMINE THE GROUND AND
SURFACE WATER RELATIONSHIPS IN THE WECOTA SANTA FE RIVER,
SEMIOLA COUNTY, FLORIDA

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This project characterized the complex variable groundwater/surface water relationships at the Santa Fe River in north-western Florida while further developing the use of the new geochemical tracer sulfur hexafluoride (SF_6) and naturally occurring radon-222 (^{222}Rn) as well as relatively established hydrologic techniques. To accomplish the objectives, mixing, water tracing, flow component and restoration experiments were completed along several reaches of the Santa Fe River and within Ocala State Park.

The mixing experiments revealed the effects of flowing springs and seeps within the stream cross section and supported more detailed sampling strategies in order to accurately estimate stream parameters. In addition, these experiments established newly developed SF_6 injection

techniques. Water tracing experiments established two things: 1) BF_3 is an excellent alternative method of ground water tracing and 2) the relationships among water sources in Glens State Park.

Flow component analysis further described the complex water balance within Glens State Park while comparing several techniques. Finally, reservoir studies confirmed the usefulness of BF_3 in determining gas exchange in karstic limestone studies.

A consequence of the research was the establishment of a first-rate BF_3 analytical laboratory, one of only a handful in North America. BF_3 has become a viable alternative to the presently used dye and harmful gases, in perhaps one of the most complicated ground water and surface water regions in the world. In addition, because this study was undertaken successfully in such a hydrologically complicated environment, future use of BF_3 in simpler environments promises to be successful as well.

CHAPTER I INTRODUCTION

The nature of active karst regions is complex and hydrogeologically difficult to describe. Claims to the historical development of a karst region are also hard to evaluate. Past studies of karst regions employ a variety of hydrologic tracers that were often scientifically inadequate or had negative side effects (White, 1960). As karst regions, in general, become increasingly populated the need to develop a reliable and environmentally safe ground and surface water tracer is obvious (Garcia Priou, personal communication, 1994). Radium bromide, a newly developed artificial tracer, provides a means to investigate ground and surface water interactions in a dependable, non-toxic manner.

Retired areas found within this region of Florida may provide new insight to the geological development of karst, both past and present. The careful study of karst and retired areas together may aid in the future planning of active karst regions. The Santa Fe River Basin in north-central Florida provides the unique opportunity to assess the relationships between ground water and river water and wetlands within a complex karstic setting.

Methods

The primary purpose of this project was to accurately characterize the complex karstic ground water/surface water relationships of the Santa Fe River while continuing to develop the use of the new geochemical tracer SP_4 and naturally occurring ^{222}Rn . The relationships between the two primary water resources, ground water and surface water, were examined in terms of their distribution using SP_4 , ^{222}Rn and other tracing techniques. The wetlands in the region were also addressed in terms of their chemical signature and connection between ground and surface water. In order to accomplish this task several goals were outlined. They included

- 1) designing and developing an efficient laboratory, injection system and collection system for the dispersal and analysis of SP_4
- 2) understanding the temporal changes of the Santa Fe River system,
- 3) understanding the mixing aspect of the river;
- 4) characterizing ground water, surface water and spring water ^{222}Rn concentrations in the study area;
- 5) locating and if not all sub-surface flow sources and sinks of ground water to the Santa Fe River within the O'Leary State Park region;
- 6) measuring river discharges and stage during high and low flow sampling periods.

Limitations

This work provides valuable information on the ground water/surface water relationships of the Santa Fe River. In

first describes the complex interactions between ground and surface water within the stream and discusses how to accurately address river sampling in a karstic environment. Surface and ground water data, used in conjunction with the river remanence data gained in this study, can assist future planners and developers of the Santa Fe River basin in managing their surface and ground water resources. This work also documents a method of interpretation for active karst regions. Methods areas studied in conjunction with intensive ground and surface tracing experiments may provide a means to interpret historical and future developments of karst features.

The research also expanded the application of SF_6 as a workable tracer in a number of complicated ground water and surface water situations. Propene, ethylene and fluoromethanes currently in use to predict ground water flow paths, flow rates, remanence coefficients, and stream mixing, are toxic or have negative side effects such as water disinfection (Adey, 1988; Quinlan, 1988). In contrast, SF_6 and ^{222}Rn are nontoxic in low concentrations, have no odor or odor and ^{222}Rn occurs naturally. For these reasons, the measurement of SF_6 and ^{222}Rn together may gain in popularity in remanence and tracer studies and possibly replace the presently used toxic gases in sensitive environments (Ellison, 1988).

An important consequence of the research effort is the establishment of a state-of-the-art SF_6 analytical laboratory. At present, only a few institutions in North America have developed the analytical capability to utilize SF_6 as a water tracer. The tracer, SF_6 , has become a viable alternative to the presently used dye and harmful gases in perhaps one of the most complicated ground water and surface water regions in the world. The techniques and ideas learned from this study will enable future researchers to study ground water in a more efficient and less harmful manner to the environment. In addition, because this study was undertaken successfully in such a hydrologically complicated environment, future use of SF_6 in a simpler environment may have high success rates as well.

Study Area

The Santa Fe River, located in north-central Florida, is a principal tributary of Florida's second largest river, the Suwannee River, which is classified as an Outstanding Florida Water (OFW) (Fernald and Patton, 1984). The Santa Fe River originates in Lake Santa Fe and Altha and flows westward until it goes underground at Gilman Sink. It returns to the surface five kilometers farther south and continues to flow westerly south and west until it joins with the Suwannee River (Figure 1). Elevations within the drainage basin of the river range from 88 m in the north;



Figure 1. Santa Fe River in north central Florida. (From Dunn and Black, 1992).

sub-basin to 10 m in the western part of the basin (Pope and Black, 1983).

The Santa Fe River basin is underlain by several hundred meters of sand, clay, silt, dolomite and limestone which unconformably overly a Paleozoic basement. The lower sedimentary rocks (Ordovician to early Eocene) consist primarily of marine limestones and some evaporites and clays, which have very low permeabilities. The sedimentary rocks (middle Eocene to middle Miocene) overlying the low permeability layer are predominantly porous limestones that comprise the Floridan Aquifer. The limestones of the Eocene Ocala Group underlie the study area and provide the source for many of the springs feeding the Santa Fe River (Figure 2; Briaud, 1978; Pope and Black, 1983).

The karstic hydrology of the Santa Fe River is extremely complex. The ground and the surface water systems in the region do not have the same geographical boundaries within this region. Although surface water does not cross the Santa Fe River basin boundary, the ground water system in the area does not coincide with the stream drainage system. Consequently, the flow of the Santa Fe River is not consistently related to the size of the drainage basin and the amount of rainfall over the basin as a whole. Both the topography and the geology are responsible for these conditions in the Santa Fe basin (Briaud, 1978; Pope and Black, 1983). Because of these circumstances, relationships

between surface water and ground water have not yet been completely resolved (Hart and Black, 1980; Wilms et al., 1979; Stewart and Wilms, 1980; Edwards, 1984).

Below the River Mile in O'Leary State Park there is a noticeable absence of surface water flowing into the Santa Fe River from tributaries. From the River Mile to the point of confluence with the Suwannee, approximately 40 known springs are visible along the banks of the lower Santa Fe (Figure 3). *Suwannea verticillata* bordering the Santa Fe provide the conduits by which precipitation flows underground to recharge the aquifer and eventually discharges into the Santa Fe River.

The potentiometric surface of the Floridan Aquifer in the Santa Fe basin is shown in Figure 4. The upstream bending of the equipotential contours indicates a leakage of ground water into the lower reach of the Santa Fe River. Water normally flows from the aquifer to the river when the surface of the river lies lower than the potentiometric surface of the aquifer. The direction of flow is reversed when the surface of the river rises above the potentiometric surface. In periods of drought the water in the lower Santa Fe River channel consists primarily of discharges from the Floridan Aquifer; while at times of heavy rainfall, the



"surface water" in the river recharges the aquifer via the springs through a process, which is known as "backflow" (Jenn and Clark, 1982; Zinnick, 1984). The spring that normally feeds the river with ground water is now acting as a conduit by which the aquifer is being fed with river water.

Physiography

This study area lies within the Western Valley and Marginal Zone physiographic provinces (White, 1977) and forms the boundary between Alachua and Columbia counties (Figure 4). To the east of Western Valley province lies the Northern Highlands Marginal Zone which is the boundary between the Western Valley Lowlands and the Northern Highlands, as described by White (1977). The Northern Highlands are poorly drained and plateau-like with elevations generally greater than 60 m above mean sea level (msl). The eastern boundary of these highlands is Trail Ridge, a sinuous, elongate feature that runs through the central part of peninsular Florida. The Ocala Scarp is the topographic marker that separates the highlands from the lowlands. This "scarp", although one of the most prominent features in peninsular Florida, was often so graded and difficult to identify through the undulating topography of the Marginal Zone.

W. I. State Park lies within the eastern extent of the Marginal Zone. The Marginal Zone has also been described by

other authors as the Transitional Zone, the hydrologic and topographic transition between highlands and lowlands (Dwyer et al., 1981) and the Perforated Zone, the area throughout which sinkholes have breached the western crest of the Northern Highlands (Macintosh, 1988). Although, the terminology represents about the same physical area, there are subtle differences between the many terms Marginal Zone, Only Scarp, Perforated Zone and Transitional Zone. The eastern boundary of the Marginal Zone is variable due to differential erosion produced by various streams and delineated by the point to which headward eroding streams have dissected the Northern Highlands (Williams et al., 1977). Its western boundary is also variable and generally depicted as the western edge of the Northern Group of sediments. The width of the Marginal Zone ranges from 2 to 11 km and elevations within this zone range from about 15 to 18 m above sea.

Within the Marginal Zone numerous streams disappear into the top of the Floridan Aquifer, including Clay Hole Creek and Ross Creek (Columbia County), and Turkey Creek and Mill Creek (Alachua County). The Santa Fe River that borders both Alachua and Columbia counties also disappears within this zone. The Suwannee River is the only stream that passes from the highlands to the lowlands without disappearing underground.

The Western Limestone, bounding the western edge of the Marginal Zone, is a weathered limestone plain. There is a noticeable absence of surface streams as most rainfall infiltrates directly to the subterranean due to extremely permeable nature. Sand and thin silt form a veneer over the fossil and barren limestone which were formerly covered by the Northern Group sediments (Parks, 1954). Williams et al. (1971) and Williams (1982) acknowledged the difficulty in assessing the cause of the degradation of the limestone plain. These workers suggest that the limestone plain may be the result of marine planation which removed subsequent sand deposits or fluctuating ground water levels retarding karst erosion processes. Remnants of the Alachua Formation and Northern Group covering the older limestone are present on outlier hills and sinkhole fill. The remnants, especially the outlier hills, are evidence that the younger units covered the Western Plate at previous times. Except for the outlier hills, most of the Western Valley has a maximum elevation of 10 to 20 ft (Parks, 1954). White (1974) named the portion of the Western Valley between the Northern Highlands and the Buckmanville Ridge the High Springs Gap. The lower Santa Fe River (below the River Rise) meanders through the High Springs Gap and separates Alachua and Gilchrist counties from Columbia county.

This karstic limestone plain was subsequently terraced by the Suwannee, Panhandle, Talbot, and Paducah runs of

Mississippian Interglacial periods (Pirkle, 1939; Clark et al., 1944). During this time period accumulations of glacial material were deposited over low lying hills and overthrust lineations (Clark et al., 1944).

Climate

The average temperatures at Lake City and Gainesville are about 18°C and 19°C respectively. The dependence of average annual rainfall on three different types of storm systems, at least in part, the high variability in annual rainfall. Annual rainfall for the period 1900-1970 ranged from 74 cm in 1928 to 212 cm in 1964 in Lake City, and from about 44 cm in 1917 to 186 cm in 1944 in Gainesville (Mason and Smith, 1963). Monthly rainfall is usually greatest from June to September. Rainfall in the basin is derived from winter fronts, local thunderstorms, and occasional tropical storms.

Geology

The following discussion of the geology of the Santa Fe basin was compiled from numerous sources, among which there is not complete agreement on the nomenclature and age of some of the formations. For more detailed discussions pertaining to the geology of parts of the basin the reader is referred to Vernon (1961), Foxi (1967), Meyer (1962), Clark et al. (1964), White (1959; 1970), Faulkner (1970) and Scott (1969).

The dominant large scale structural features in north-peninsular Florida are shown in Figure 3. These features include: the Peninsular Arch, Ocala Plateau, Jacksonville basin and Appalachian Embayment (Ruscha, 1961; Gerych et al., 1968; Miller et al., 1978; Scott, 1980; Spighe et al., 1984). Of these, the Peninsular Arch dominates the distribution of Mesozoic sedimentary rocks throughout this study region.

The Santa Fe River basin is underlain by several hundred meters of partially consolidated marine and nonmarine deposits of sand, silt, clay, gravel, limestone, dolomite, and dolomitic limestone. The interpretation of electric logs of test wells indicates that 0.85 to 1.48 km of sediments, ranging in age from early Cretaceous to Eocene, unconformably overlie structurally high, complex basement rocks of Paleozoic age (Figure 4 and 5). The lower sediments (Cretaceous to early Eocene) consist primarily of marine limestone, some evaporites and clay, and they have very low permeability. These rocks form a basal aquiclude which effectively prevents the further downward movement of ground water.

The sedimentary rocks (middle Eocene to middle Miocene) overlying the basal aquiclude are predominantly porous marine limestones which serve as the principal water-bearing units in the area that comprise the Florida



Figure 3. Structural features in peninsular-north Florida (after Siddons, 1993).



Aquifer. The Floridan Aquifer underlies all of the Santa Febedia and it is the principal source of many of the springs on the lower Santa Fe River.

An upper aquiclude of sand and clay sediments overlies the limestone units in the eastern half of the basin. These sediments are early-to-middle Miocene in age and they generally have low permeability, serving to confine the water in the Floridan Aquifer under artesian pressure. Locally, some limestone beds within the unit are tapped for domestic water supplies.

Above this unit, sediments of coarse sand and clay (late Miocene to Pliocene) serve as a temporary storage reservoir for water which seeps slowly into the semi-confining beds of the aquiclude. This secondary, or water-table aquifer, is usually under non-artesian conditions and is recharged directly by local rainfall which percolates quickly through the topsoil. The water-table aquifer yields moderate quantities of water to shallow wells in those areas of the Northern Highlands where it exists.

The Tertiary strata which compose the Floridan Aquifer in the Santa Fe basin have been divided into several series on the basis of their age and their position in the stratigraphic column (Table 1). The lowest series (Bosque) includes the Olsamer Limestone, Lake City Limestone, Arco Park Limestone, and the formations of the Basin Group.

Table 1. Regional stratigraphy in Northeastern Alachua County, Florida (after Middlebrook, 1993).

Age	Period	Epoch	Description of Group	Characteristics
Q C T M P	Tertiary	Quaternary	Recent to Pleistocene and Pliocene	loesslike fill, Florida terraces, and thin partial sand (Q), fine to medium grain sands with minor organic and heavy minerals
		Pliocene to Miocene	Alachua Formation	deep to blue-grey clayey sand that weathers red-brown (P); siliceous fill and medium to coarse granitic lacustrine deposits with limonite concretions and pebbles (Q)
		Middle to Lower Miocene	Hawthorn Group	Pinnacella clayey sandstone along with varying amounts of Pella sand and northward (N) clayey formation described but difficult to map locally (M); few Alachua-type mapped to study area (P)
		Oligocene	Swannan Limestone	very pale yellow, moderately indurated, brown (brownish) carbonate (O); Alachua-type mapped
		Eocene	Oriskany Limestone	white to cream, soft & granular, massive to silty (E); limonite, locally with indurated (O); Lehighville sp.

The oldest unit which bears fresh water is probably the Glenside Limestone (early Eocene), but its permeability is generally low and the sulfate concentration is high. The high sulfate content of the Glenside Limestone causes it not to be considered an important contributor to the Floridan Aquifer. The top half of the unit is a moderately porous brown limestone with some oysters and nautilus. The bottom of the column, however, is strongly dolomitized, and the water therein is highly mineralized and unsuitable for domestic use. Over most of the Santa Fe basin, the Glenside lies at relatively great depths (400 meters to 500 meters below the surface).

The Lake City Limestone (middle Eocene) is the youngest formation in the area from which supplies of fresh ground water may be obtained. This unit is about 100 meters thick and is composed of alternate layers of dark brown dolomite and chalky white limestone, both of which contain oysters and nautilus. The permeability of the unit varies from low near its base to high at the top, and the entire formation is considered a part of the Floridan Aquifer, but very little is being pumped from the Lake City Limestone because of its high sulfate content.

The Arroyo Limestone (late-middle Eocene) disconformably overlies the Lake City limestone, and is a cross-bedded, chalky deposit which is 10-60 meters thick and has a distinctive and abundant fauna of bivalves. The Arroyo

Park limestone is a highly permeable part of the Floridan Aquifer, but it is not extensively tapped as a potable water supply because of its high sulfate content. The Sidney, Lake City and Archaean limestones do not outcrop within the Santa Fe basin.

The Ocala Group (late Eocene) disconformably overlies the Archaean Park limestone. The group consists of three formations of very similar lithology. From oldest to the youngest they are the Inglis, Williston and Crystal River Formations. The limestones of the Ocala Group vary from a porous, cream-white, loose conglom of large boulders and shells to a brown, micaceous ridged, ochreoid-rich limestone. The total thickness ranges from 40 to 70 meters. Locally, limestone at the top of the Ocala has been replaced with chert. The permeability of these formations is extremely high and the Ocala Group serves as the principal source for many of the springs and large capacity wells in the Santa Fe basin.

Limestones of the Ocala Group, the oldest rocks exposed in the Santa Fe basin, are commonly found at the surface west of High Springs along the channel of the lower Santa Fe River; the outcrop is covered in the area only by a veneer of loose sand. A well developed karst topography, which includes such features as filled open sinks, sinkhole lakes, solution pipes, basins and prairies, is typical of areas underlain by the Ocala Group. The karstic features

pattern of the limestone has produced a one-meter water rapid on the river near Fort White. The strike of the fold is approximately E. of N., which conforms to the general fracture pattern of northern Florida.

The Oligocene Series, represented by the Suwannee Limestone, unconformably overlies the Crystal River Formation. The Suwannee Limestone is very permeable and porous and is lithologically similar to the members of the Ocala Group. The Suwannee is composed of hard and soft beds of white, tan, or green-colored limestone that are partly dolomitic and oolitic; some sand and silicified layers of shert are also present. The Suwannee is a residual sediment which is generally absent in the western half of the Santa Fe basin; it occurs locally north and northeast of Deltonville, and appears to be continuous in a narrow outcrop northwest of Silver State Park. The thickness in this area reaches 15 meters.

The Miocene Series is represented by the Hawthorn Group and Alachua and Ocala formations (Scott, 1949). The Hawthorn Group, in the study area, consists of three formations, (the Ocala, the Alachua and the Hawthorn). The Hawthorn Group is composed of marine sands, clays, silt and sandy limestones, all of which may be phosphatic. The lower part of the Hawthorn contains beds of hard dolomitic limestone and interbedded clays, and the contact with the underlying formation is probably unconformable. The main

deposit reaches a thickness of 75 meters and consists chiefly of thick clays that range in color from yellow-green to light-gray. Layers or lenses of hard and soft white limestone and phosphatic limestone are interbedded with clays; large pebbles of phosphate having brownish-black color are disseminated throughout the formation.

Though the Northern is continuous over much of the Santa Fe basin, the main body of the deposit lies in the Northern Highlands province along the upper course of the river. The outcrop in this area is often covered by a relatively thin layer of loose sand, sandy clay, and organic humus. Remnants of the Northern have filled sinks and lake basins and have forced a mantle of sediment over the outcrop of the Coala Group in some parts of the western basin. The relatively thick and impermeable Northern sediments serve as the principal confining beds to contain the waters of the Floridan Aquifer under artesian pressure. In addition, these semi-confining beds serve as a basal aquitard for the shallower water-table aquifer, restricting the movement of this water into the aquifer below. The Northern Group is itself an aquifer and yields small quantities of water to domestic wells in the eastern sections of the Santa Fe basin, but its permeability is generally low and the chemical quality of the water it produces is usually poor at depth.

The Chaptawhatchee Formation overlies the Hawthorn along the extreme eastern parts of the Santa Fe basin, but it does not crop out anywhere within the area. Thin beds of sand and limestone are interlayered with soft yellow fossiliferous clay and partly-indurated sand. Pebbles of phosphate and silica are disseminated in these beds, and mollusk shells are abundant throughout the formation. The thickness of the Chaptawhatchee Formation in the basin is only about four meters, and it is of minor importance as a hydrologic unit.

The Alachua Formation (late Miocene to early Pliocene) is a terrestrial deposit of reddish-white sands interbedded with various colored clays, sandy clays, and pebbles of phosphate. Siliceous limestone and phosphate boulders are scattered throughout the formation, as are organic materials and the fossils of various types of land vertebrates. The sandy clay and sand beds of the Alachua Formation are not as calcareous and phosphatic as similar beds in the Hawthorn, though phosphate deposits are mined in the Fort White area near the confluence of the Santa Fe and Ichauway rivers. The Alachua Formation reaches a thickness of 18 meters and crops out near the south bank of the river along the Alachua/Gadsden county line. The Alachua acts in conjunction with Hawthorn as a semi-confining unit to retain water in the Floridan Aquifer, although the aquifer is often exposed in the area of the

outcrop due to the collapse of caverns in the underlying Ocala Group. In areas where this sinkhole development has been extensive, direct recharge to the Floridan Aquifer from local rainfall is common.

Recent clastic sediments, the Ocala Sand Formation, of late Miocene age were deposited in the Northern Highlands of the Santa Fe basin as lacustrine at different stages of sea level. These deposits comprise the prominent topographic features of the region, and they overlie much of the older sediments in the area. Two lithologic units are discernable: one predominantly sand and the other predominantly clay. The sand unit is mostly fine grained and argillaceous at the surface but coarsens with increasing depth, and large pebbles of phosphate quartz are found at its base. The sands are dark brown or black due the presence of organic matter and iron-bearing materials. This unit ranges from 4 to 14 meters in thickness. The clay unit is mottled red to yellow-gray and ranges from two to five meters in thickness. The clays are generally in the upper part of a sequence of beds which overlie green-colored sands and sandy clays. The total thickness of these sediments reaches 18 meters in the northeastern parts of the basin.

Pleistocene and Holocene fluvial deposits of clay, sand and gravel usually occur beneath the flood plains of the Santa Fe and its tributaries. The stream bed of the lower Santa Fe, however, is primarily exposed limestone veneered

with coarse sand. Deposits of peat and silt are being formed in the bottom of plugged sinkholes, lakes and swamps in the basin. Saline dunes of fine sand generally occupy the higher topographic elevations, and thicker lenses of wind blown sand occupy the valley floors and form the principal shallow surficial aquifer in the Northern Highlands.

The western part of the Santa Fe River consists of a well developed barot plain with exposed Tertiary limestone, comprising the Floridan Aquifer. The Floridan Aquifer is mostly unconfined here because the Southern Group has been removed by erosion (Pett, 1957; Driel, 1970; Farnold and Pett, 1981a Figure 7). Except for the Santa Fe and Interoceanic Rivers, and Coy Creek (intermittent), the western sub-basin lacks surface discharge. Several large springs contribute baseflow to the lower Santa Fe River (Figure 7). Ground water inflow also occurs within river bottom swamps that are controlled by large joint fractures found within the aquifer. Unfortunately, the detection of such sources of ground water delivery to the river is very difficult due to the depth of the river and the dark color of the water (Hess and Clark, 1980). Ground water from the Floridan Aquifer adding to the lower Santa Fe River modifies the chemical parameters of the river and is indicated by increasing pH, alkalinity, specific conductance, and decreasing temperature (Farnold and Pett, 1981a).



Figure 9. Hydrogeologic units of the western Santa Fe River Basin (after Bush and Black, 1992).

Basal Development

Because basal facieses in this study region, a brief description of its evolution and type is necessary to understand the ground water and surface water interactions. The Florida Platform encompasses the Florida Peninsula and parts of the Southeastern Atlantic and Gulf Coastal Plain. Including the adjoining continental shelves, the Florida Platform has been primarily a carbonate platform on which thousands of meters of dolomite and limestone have been deposited with relatively minor amounts of evaporite and silicic sediments for much of the Mesozoic and Cenozoic periods (Clark et al., 1984; Beck, 1989).

The carbonate rocks of the Florida Platform have been variously subjected to repeated cycles of sea level fluctuations (White, 1988; Swenson and Beck, 1979; Swenson and Glass, 1984; Ford and Williams, 1988). Sea level and its changing position is considered to be the keystone in the development of basin processes due to its repeated shift from ridges to phreatic zones (Beck et al., 1984). The origin of numerous subsurface karstic features on the Florida Platform is also attributed to glacio-eustatic sea level changes (Jordan, 1984; Jordan et al., 1984; Bailey and Bailey, 1974; Denbury, 1977; Dogli et al., 1980; Hubert 1985; Popescu, 1988; Mallin et al., 1988; Teichelli and Parnell, 1988; Pauli et al., 1987).

There are primarily two types of karstic evolutionary schemes (Ford and Drees, 1978). The first theory employs generalized models of the origin and sequence development of karst landforms. The second theory describes regional denudation chronologies in which the history of karst landform is reconstructed (Burr, 1984).

Grand (1934) and Powell (1978) based their early theories of karst on the geomorphical cycle concept and the sequential development of both surface (epikarst) and underground (endokarst) landforms. This type of development is in contrast to more recent author's theories such as Ford and Drees (1978) who considered the development of epikarst and endokarst landforms separately. By doing so, Ford and Drees (1978) have resolved most of the contradictions in development found the earlier papers of Grand (1934) and Powell (1978). Walton (1983) supports Ford and Drees and their theories of karstic environments that support separating the epikarst and endokarst development. To support these authors, numerous studies of closed depressions (dolines) have shown that since dissolution proceeds from the surface downward, there is little, if any, genetic relationship between the surface karst and the underground landforms (Williams, 1973; Jennings, 1978; 1981; Palagouas, 1979).

Within the western Santa Fe River basin, both epikarst and endokarst interactions as well as paleokarst phases

affect the development of karst in the region. Springfield and others (1979) concluded that the vertical movement of water from the surface through joints, fractures and other openings in the Tertiary carbonate rocks of Florida, to discharge areas initiated the formation of internal dissolution channels causing a circulation system below the water table. As base level and the top of the saturation zone were lowered, accompanying sinkholes developed in the initial stage of karstification because of the previously karstified underlying carbonate rocks (Springfield et al., 1979).

In contrast to these sinkhole laden areas there are subregions within the western river basin where previously existing dolines and dissolution shafts extended many meters below present day sea level. These sinkhole regions are now buried because of the present higher water table. This higher water table is the result of increases in sea level caused by Pleistocene deglaciation. This increase in sea level resulted in the zone of saturation to rise to water levels in the limestone at or above the bottom of the dolines that form in the zone of saturation. (Hallward and Labaree, 1975).

White (1982) believes that the karst topography created by previous emergent episodes has been buried by the sands deposited during interglacial times of high sea level. These karst features, although sometimes difficult to

identify and analyze due to the brevity of glacial stages compared to the interglacial stages, can be attributed to ground water circulation in the Florida Platform which is the product of several cycles of substantial exposure.

Bigger and smaller solution openings should be encountered with increasing substantial exposure of the continental shelf. The decrease in solution openings occurs because surface elevation decreases. This surface decrease in turn causes the total length of time as well as number of times the area will be eroded and exposed to subaerial conditions to decrease. Thus, during interglacial stages of water climate, sea levels were higher, and solution was probably retarded in the lower coastal areas because the openings were largely filled with sediments and salt water which has less capacity to dissolve limestone. White (1948) states that the coastal plain itself should be most eroded on the highest land surfaces. White's theory of more developed karst in higher regions is represented in this study area. The most active karst regions in the western Santa Fe River basin are found along the marginal zone marking the boundary between the coastal lowlands and the central highlands physiographic provinces, where elevations are generally above 70 meters in elevation.

With prolonged re-emergence of the Florida Platform the reactivation of the karst cycle slowly opened new avenues of underground discharge and the planimetric surface gradually

dropped. This seems to have occurred in the western Santa Fe River basin where disappearing lakes, disappearing rivers, and abandoned spring heads all suggest such a drop (White, 1984).

The basin development and evolution on the Floridan pediculus was a complicated and intricate interaction of surface and ground water interactions as well as the overriding influence of the basin base level, sea level. The basin's complicated nature is evident today in the surface and ground water interactions found within the western Santa Fe River Basin.

Regional Ground Water Flow

The general trend of ground water flow in the western portion of the Santa Fe River Basin is in a westerly to north westerly direction (Rum and Black, 1981; Fernald and Pettus, 1981; Nash, 1984). The Floridan Aquifer discharges to the Santa Fe and Emburytown Rivers, via springs near the rivers where the potentiometric surface is near land surface. Discharge from the Floridan Aquifer also occurs through wells and evapotranspiration. Recharge to the Floridan Aquifer occurs via springs within the Santa Fe River and through predominant point recharge regions as also does from throughout the landscape physiographic provinces (Rum and Black, 1981; Fernald and Pettus, 1984). Because there is a lack of surface streams other than the Santa Fe

and Ichaukeese rivers, almost all the water they receive the ground surface flows as ground water through this region.

Based on a survey completed by the Immokosee River Management District (1988), the potentiometric surface of the Floridan Aquifer is approximately 18 m (60 feet) below O'Leary State Park and drops to less than 5 m (15 ft) where the Santa Fe River and Ichaukeese rivers join.

Wetland Hydrogeology

The hydrogeologic component of wetlands is considered to be the most important component to the wetland environment because it ultimately controls the type of soil that will form and the type of vegetation that will grow in an area. However, it is often the least understood and the most difficult to determine. For example, water flow rates through the soil in wetlands vary several orders of magnitude (Table 1).

Most of the wetlands that border the Santa Fe River have been classified as bottomland hardwood wetlands or riparian wetlands (Ritch and Gosselink, 1988) or a palustrine forest (Vowles et al., 1978). Some upland forest are found in the study area especially throughout O'Leary State Park. These areas have a different type of hydrogeologic regime than the riparian wetlands that control

their existence. For the most part, the chemical composition of these wetlands will be addressed in order to better establish the wetlands' possible connections with other water sources in the region. In actuality, very little is known about the quantity and quality of wetland water added to the riverine environment in many areas (Richey and Scudlark, 1984).

Table 2. Hydraulic Conductivities of Wetland Soils Compared to Other Mineral Soils (from Hatch and Goodrich, 1985).

Location or Soil Type	Hydraulic conductivity cm/year $\times 10^3$
Maritime Freshlands	
Highly forested Piscataway Bog, D.C.	2-22-2,000
Sw. S.S.S.S. slightly decomposed	500
moderately decomposed	50
highly decomposed	1
Coral Is., U.S.S.S.S. 2-50 cm deep	100
100-150 cm deep	1
South American Freshlands	
(general)	
clay	>100
silt	1.0-100
sand	0.1-0
Coastal salt marsh	
Great Saltwater Marsh, MA (measured conductivity)	
0-30 cm	1.0
high permeability zone	1,000
sub-foot transition zone	0.1
Mar-Quat Wetland soils	
Cypress Lake, FL clay with minor sand and silt	0.01-0.1 20
Blackwater Swamp Wetland, GA	2.0-200
Mineral soils (general)	
Clay	0.05
Limestone	0.0
Sand	5000

CHAPTER 2
BACKGROUND

Radon-222 (^{222}Rn)

Radon is an inert, volatile gas occupying the third place in the noble gas group of the periodic table. It is the heaviest known gas with an atomic number of 86 and atomic mass of 222. ^{222}Rn , with a half-life of 3.823 days, is the most abundant of the three predominant alpha emitters and is naturally derived from radium-226 (^{226}Ra half-life $\approx 1.6 \times 10^3$ years). Both ^{222}Rn and ^{220}Rn are part of the uranium-238 decay series. Uranium-238 and ^{226}Ra are common constituents in continental sedimentary rocks and sediments (Rip, 1961; Elison et al., 1969, 1970). As ^{222}Rn decays naturally to ^{218}Po , in a closed system, 99 percent equilibrium between ^{222}Rn and ^{218}Po concentrations will be established within approximately 15 days (Rogers, 1950; Elison 1969; 1970; Ashkinos, 1961).

Because ^{222}Rn is highly soluble in water and a volatile gas it will reside in the aquifer to decay to lead-206 or once released to the surface, will be absorbed in the atmosphere where it exists in low concentrations (Riesinger and Rogers, 1961; Rogers, 1958). Three physical properties, the short time duration required to establish equilibrium

between ^{222}Rn and the parent nuclide ^{226}Ra , the volatility of ^{222}Rn in continental sedimentary material, and the volatility of naturally occurring gaseous ^{222}Rn , make ^{222}Rn a commonly used natural tracer with many applications (Foster et al., 1967; Kay, 1969; Illies, 1969).

Rogers (1958) was the first to use ^{222}Rn to investigate the relationship between ground water and surface water. Rogers determined that ^{222}Rn concentrations in a Snake Mountain, Utah, flowing stream will be low due to the volatility of the gas and the slow decay rate of the radionuclide that may be contained in rock and sediment in the stream channel. Furthermore, he demonstrated that ^{222}Rn concentrations in ground water from springs was much higher than those in surface water. Also, the spring water was identified as the source of ^{222}Rn in the stream.

Rogers' initial study has led to many advances in the usefulness of ^{222}Rn in hydrogeological problems (Foster, 1969; Brander et al., 1967; Jacoby et al., 1970; Fleming et al., 1967; Illies, 1969; 1968, 1969; Illies et al., 1968). Subsequent studies by Illies (1969) and Illies and others (1969) corroborated Rogers' work. They described the low levels of ^{222}Rn in a Snake and Pacific River stream as a function of the loss of ^{222}Rn to the atmosphere and the high levels of ^{222}Rn due to the input of ^{222}Rn enriched ground water. Figure 8 depicts the relationship between surface and ground water ^{222}Rn levels in a Pacific River stream.

Initial measurements of background ^{222}Rn concentrations of about 10 dpm/l in the Santa Fe River have been performed. Also, spring ^{222}Rn concentrations were measured at levels about 1400 dpm/l for the lower Santa Fe River basin (Figure 18). Using these values, the ratio of ground water ^{222}Rn concentrations to stream levels is 100:1 (Ellis et al., 1972). Because this ratio is so high, ^{222}Rn provides a sensitive means of detecting ground water inflow to surface flow that no other naturally-occurring chemical in ground water and surface water can compare (Ellis, 1968).

Radon Saturation (SF_6)

Wanninkhof (1968) employed SF_6 as a gaseous tracer to study the gas exchange rates across the air/water interface in three lakes. In addition, he included an in depth discussion of the physical properties of SF_6 and its analysis. To date, his work is the most thorough and detailed employing SF_6 in the hydrologic field. The following will provide a summary of his data pertinent to this investigation. The interested reader is directed to read Wanninkhof (1968) for more detailed information.

SF_6 is a volatile, artificial, nontoxic, inert gas, that can be detected by electron capture detection methods due to SF_6^{19}F ions following the procedure of Wanninkhof (1968) and (Ellis, 1968). The molecular weight of SF_6 is

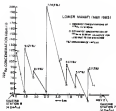


Figure 6. Rio Grande do Brazil, ^{222}Rn concentrations (JLLI, et al., 1995).

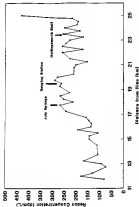


Figure 50. Relative Chlorophyll Concentration.

164.08 g. It has a vapor pressure at 21°C of 11.4 atm and has an extremely low solubility in water at 5.4 $\text{cm}^3 \text{ SF}_6/\text{kg}$ (Mannickhof, 1944). Mannickhof (1944) reports that SF_6 has an atmospheric background level of about 1.5 parts per trillion by volume. This value has not significantly changed over the past eight years (Wilson and McKay, 1971). Water in equilibrium with air will have a concentration of NaCO^{H} mol/L (Ellis, 1948). SF_6 is not considered dangerous because a maximum limit of 1000ppm is considered harmful to humans and expired samples usually contain less than 0.5ppm of SF_6 (Mannickhof, 1944).

The difficulties associated with SF_6 as a tracer are its affinity for certain porous substances, its ease of contamination and contamination of SF_6 with other gases during analysis (Ellis, personal communication, 1971; Mannickhof, 1944). Materials such as rubber, plastic, grease, and talc cannot be used in lines, containers, and extraction and analysis equipment because of their affinity for SF_6 (Mannickhof, 1944). Steel, copper, glass and nylon tubing were used exclusively in these experiments and are not prone to absorb SF_6 (Mannickhof, 1944). Because small amounts of SF_6 were used in this study, 99.999 pure SF_6 standards of SF_6 (1ppm, 40ppm, 100ppm) and expired samples were kept in different rooms at all times, except during analysis of water samples, to avoid cross-contamination of the SF_6 . Contamination with even minuscule

and synthetic humic acids can pollute air to such an extent that analysis becomes impossible (Wassinkhof, 1960). Because of this, no aerosols, lubricants, or petroleum products were allowed in the analysis lab or near sample containers.

The Schmidt number (kinematic viscosity of water divided by the diffusion coefficient of the gas) is about the same for both SF_6 and ^{85}Kr (Wassinkhof, 1960; Ellis et al., 1964). Because these Schmidt numbers are similar, gas transfer velocities for both gases in a stream will be the same (Ellis et al., 1965). Therefore, the dual application of ^{85}Kr and SF_6 allows for the more accurate description of surface and ground water interactions. Details of their application can be found in Ellis and others (1964) and Ellis and others (1966). Briefly, the dual tracer work allows for the accurate detection of ground water springs or seeps and the quantification of its input to the stream.

Most recently SF_6 has been shown to be "conservative" tracer in simple laboratory experiments revealing its inert properties with respect to adsorption to saturated sandy material (Ellis and Weiler, 1960). In this experiment however, the SF_6 can only be labelled conservative because the sandy material through which the SF_6 was pumped was enclosed within an acrylic tube. Essentially the experiment was run under closed conditions with respect to the atmosphere, depicting SF_6 as being conservative.

Radiation-RT

Perhaps the most widely used tracer in burst tracing are fluorescent dyes. These dyes are commonly used because they are readily available, and they all, to some degree, are absorbed on activated coconut charcoal or unleached cotton. Fluorescent dyes are generally superior to non-fluorescent dyes because they can be detected at concentrations ranging from one to three orders of magnitude less than those required for visual detection. Thus, tracers with fluorescent dyes usually can be completed without the aesthetically unpleasant probability of disclosing a private or public water supply.

Because tracing burst ground water flow frequently involves either private or public water supplies, the problem of toxicity of the tracers must be considered. There is a relatively large amount of information available on the toxicity of the most common tracers. Smart (1964) presents a review of the toxicity of 18 fluorescent dyes used for water tracing that includes the tracers discussed in this manual, namely, rhodamine WT, optical brighteners, Rhodol Yellow 6B, and fluorescein. As reported by Smart, these dyes present almost carcinogenic and mutagenic hazards: Rhodol CBS-2 (brightener), fluorescein, and rhodamine WT. Douglas and others (1964) reported that rhodamine WT is non-carcinogenic but found a small but statistically significant dose-related, mutagenic effect.

However, they concluded that the use of rhodamine WT does not appear to represent a major quantum hazard.

Steinkamp and Johnson (1988) have shown that, under ordinary dye study practices in surface waters, the possible formation of carcinogenic nitroamines from the use of rhodamine WT should not constitute an environmental hazard. In ground water, which may be enriched with nitrite, nitroamines could form, but high-nitrite concentrations in ground water are uncommon (Cass, 1985). Therefore, the possible formation of nitroamines is not likely to be a problem (Wall et al., 1988). Quinlan (1987) points out that numerous investigations (Miller and Miller, 1975; Lyons et al., 1975; Cass et al., 1976; Burg et al., 1977; Smart, 1984) have found optical brightness to be nontoxic, non-carcinogenic, and non-mutagenic and therefore safe for use as a tracer. It should be pointed out the dye, Rhodamine B, which was earlier approved by the EPA for use as a tracer in pesticide water (Heitman, 1980), is no longer recommended because impurities within it are known to be carcinogenic and possibly mutagenic (Smart, 1984).

Although many different fluorescent dyes are used as ground water tracers, present usage is centered on four: rhodamine WT (E-60 Acid Red 144), fluorescein (E-1 Acid Yellow 199), optical brightness and Direct Yellow 22. In general rhodamine WT is not used for qualitative tracing because of the difficulty of visually distinguishing the pink color of

the dye from that of other organic compounds that can be easily be worked by activated coconut charcoal (Wall et al., 1944). However, it is considered an ideal reagent in quantitative settings under specific hydrologic conditions, even though no fluorescent traces in 100 percent conservative because some dye is lost to sorption or chemical decay (Wall et al., 1944). Therefore, dye loss must be considered during quantitative analysis of the dye-recovery data. The advantages are that it is photochemically stable and can be used in low pH waters. The disadvantages include the following problems: the detection may require fluorometric analysis, it is moderately adsorbed to clay particles and is difficult to distinguish in qualitative tracing. The open detectable limit is about 0.51 micrograms per liter. In most natural settings, with a fluorometer which is about one to two orders of magnitude lower than the other popular used tracers.

Oxygen Isotopes

Naturally occurring oxygen is composed of the stable isotopes ^{16}O , ^{17}O , and ^{18}O . The ratio of ^{16}O to ^{18}O in air is about 1:489; however, in nature this ratio can vary by about 10%. Many chemical and physical processes in nature are accompanied by oxygen isotope fractionations.

During phase changes between liquid and gas the heavier water molecules tend to concentrate in the liquid phase, which fractionates the oxygen isotopes. Water that evaporates from the ocean is isotopically lighter than the water remaining behind, and precipitation is isotopically heavier; that is, precipitation contains more ^{18}O than the vapor left behind in the atmosphere.

The use of mass spectrometry can determine the ratio of isotopes in a water sample. These isotopic ratios from an environmental water sample can be compared with the isotopic ratio of standard mean ocean water (SMOW). The comparison is made by means of the parameter (δ), which is defined as

$$\delta^{18}\text{O} (\text{‰}) = \frac{[^{18}\text{O}/^{16}\text{O}]_{\text{sample}} - [^{18}\text{O}/^{16}\text{O}]_{\text{SMOW}}}{[^{18}\text{O}/^{16}\text{O}]_{\text{SMOW}}} \times 10^3 \quad (1)$$

(Feller, 1981).

Ground water in this region within the Floridan Aquifer has a relatively constant value of about +4 parts per mil, relative to (SMOW) (Paul Gessert, personal communication, 1992). In shallow ground water systems with normal temperatures, the concentrations of isotopes are little affected by chemical processes. Once the water moves below the upper part of the soil zone, the ^{18}O concentration becomes a characteristic property of the subsurface water mass. Surface water, on the other hand, has varying concentrations of ^{18}O due to the addition or mixture of

precipitation with different ^{18}O concentrations and evaporation effects can change the overall nature of the ^{18}O signal. Because of differences in the ^{18}O content observed in ground water and surface water, mixing between the two water masses can be estimated.

Stable oxygen isotopes of the water samples were analyzed using an initial process of equilibration of CO_2 gas in a shaker bath at 25°C . The CO_2 gas was then distilled off line using a methanol and dry ice slush mix and liquid nitrogen trap. The CO_2 gas was then sealed in six millimeter vacuum-press glass tube for transfer to the VG-Laser Fricke Series 2 mass spectrometer for analysis. Precision of internal standard was 0.1 per mil (Bass Model, personal communication, 1983).

Water Concomitants

As precipitation reaches the ground in a watershed, it will either infiltrate into the ground, pass back to the atmosphere through evapotranspiration or flow on the surface as runoff. When enough runoff comes together, possibly combined with ground water flow the mineral content is already different from that of the original precipitation.

Because of the differing geologic, atmospheric, and human environments there is no typical water quality for surface and subsurface flows (Giblin and Gosselink, 1984). Wetland environments, however, are the sources, sinks and

transformers of elements for various trace metals, particularly iron, manganese and sulfur, which make their chemical signature distinct from other water environments (Richey and Gosselink, 1987).

Due to the fact that elements should differ from one water environment to the next, and the fact that there are multiple water sources in the region, cation concentrations were measured in water samples taken from the two major water components of the area, stream flow, and ground water. Wetland/riparian water was also sampled throughout O'Leary State Park. Primarily aluminum, calcium, sodium, potassium, and magnesium were analyzed by atomic absorption techniques to distinguish between environments. These elements were analyzed because there is abundant background information on them and they typically are used in conjunction with one another to distinguish between different water bodies or sources (Fetters, 1988). For example trilinear diagrams with Mg^{++} , Ca^{++} , and $\text{Na}^{+}\text{K}^{+}$, as their corner points are used to classify magnesium, calcium, and sodium or potassium type natural waters (Fetters, 1988).

The major cation species in most natural waters are Na^{+} , K^{+} , Ca^{++} , and Mg^{++} . The ground water chemistry of the Floridan aquifer in this region has been well established as has the chemistry of the Santa Fe River (Benn and Black, 1982; Katz, 1984). The two bodies are chemically distinct at the mixing point of the Santa Fe River at O'Leary sink

because the river at this point is a surface fed stream, driven by precipitation events. Because the Floridan Aquifer material is primarily limestone, the ground water chemistry reflects the dissolution of the aquifer material. The dominant cation in ground water is Ca^{++} , which has a concentration about 10 times that of the upstream Santa Fe River (Paine and Mack, 1983; Eitz, 1983).

Because there are at least two chemically distinct water bodies, mixing of these water masses through the region will indicate sources and sinks of ground water, river water and possibly surface water to and from the river system.

Previous Hydrogeological Investigations

Records of stream flow in the basin have been collected by the U.S. Geological Survey at various points in the area since 1907. These records were published annually in a series of water-supply papers, and a summary of these records through 1968 is published in Water Supply Paper 1324 (1971). Smith and Brown (1981) gave information about the chemical quality of water in the area and other parts of Florida.

Salvin (1949) provided the most detailed description of the Ocala State Park area as he attempted to determine the location of the underground flow path of the Santa Fe River. Although his work never conclusively determined the

underground path, it did make some significant contributions to understanding this basin. The focus of the work was hydrogeological mapping of the state park. Also included in his work were the first published bathymetric maps of the park's numerous sinks. Shirvin's major contribution to the hydrogeological aspects of the park was the observation that water remained flowing from the River Basin even though the upstream section of the Santa Fe River was dammed due to construction. This piece of information is significant because it reveals that the under ground flow path of the Santa Fe River through O'Leary State Park has ground water contributing to its flow before it reaches the River Basin. He also noted a significant "clearing up" of the water found within the sinks and at the River Basin during this damming period.

Brice's (1978) application of $^{222}\text{Rn}/^{222}\text{N}_2$ to the characterization of water sources in the lower Santa Fe River basin permitted the identification of three different water types within the basin. Using this finding he characterized the springs along the Santa Fe River as being one or a combination of any water types and then identify different source regions for the Santa Fe River. His work has recently been disputed because springs which he believed to be unconnected have since been directly linked through cave diving explorations (Rinold, 1984). Rinold (1984) was

able to gain through conduits that directly linked the two adjoining caverns Beebe's Bar and Jolly Springs.

The next phase of investigation into this region was undertaken by Kane and Slack (1973). This comprehensive report characterized nearly every aspect of the water resources within the Suwanee River basin. It revealed the quantity and quality of the surface and ground water in the region as well as their distribution. The paper concluded by discussing the potential for future development in the region from both a surface and ground water perspective.

Even though this paper was detailed and extensive it did not make connections between hydrologic aspects and geologic characteristics. Best (1984) provided some insight to the connections between karst and the geologic nature within the northern peninsular region. His guidelines indicate numerous exposures within karst features as well as interpretive relationships between stratigraphy and the surrounding karst.

Widjerski's (1988) research into the Suwannee's sink region just north of Ocala State Park also gives general background information on the region. In addition he provides an in-depth probe into the relationships among surface water, ground water (the multiple aquifers) and precipitation along the body of water found in this active karst region.

Restoration Coefficients

Streeter and Phelps (1925) defined the restoration coefficient as a first order rate constant in the basic absorption equation for water. The restoration coefficient in a natural stream is a general measure of gas exchange capacity and includes the effects of molecular diffusion and mechanical dispersion (mixing) (Hargrett and Coffin, 1969; Eilins et al., 1974). Although the restoration coefficient is generally reported as a single constant, the single value actually represents an average of many individual values within the stream reach (Tobocqun, 1967).

Water quality managers use these restoration values and dissolved oxygen (DO) models to estimate the capacity of a stream to sustain organic loadings from natural or manmade sources. The self-cleaning capacity of a river is directly related to the DO levels and the ability to replace oxygen removed by the reduction of organic wastes. The restoration process is primary in controlling the negative effects oxygen-demanding substances (Hargrett and Coffin, 1969; Parker and Gray, 1977; Tokutake et al. 1984). Methods for the accurate and dependable evaluation of stream restoration capacities are a valuable tool in the determination of waste-load allocations and waste-treatment requirements.

A variety of methods for the determination of stream restoration coefficients have been proposed. These include the dissolved oxygen balance technique, the disturbed

equilibrium method, gas transfer techniques, and various predictive mathematical models (Stephan and Cuffin, 1989; Riddison et al., 1979; Parker and Ray, 1993; Yamanaka et al., 1994). All of these methods have limitations. For example predictive models sometimes yield unreliable results and gas tracer measurements may be expensive and logistically difficult to carry out (Bennett and Riddison, 1977). Since its development, however, the gas tracer method has been considered the most promising and reliable method (Tsigolias and others, 1989; Riddison et al., 1979; Ellis et al., 1994). This method had gained further acceptance since the introduction by Riddison and others (1976) of a modification of the method which uses hydrocarbon gas tracers instead of the radioactive tracer krypton-85 (Tsigolias et al., 1985).

To find respiration coefficients, other workers have experimented with a variety of gaseous tracers, including natural ^{222}Rn (Ellis et al., 1994; and Hinkley and Moore, 1981) freon-12 (Riley and Howard, 1984; Wilcock, 1994; 1988), and SF₆ (Wanderschoof et al., 1988; Ellis et al., 1994). The currently accepted technique for measuring respiration involves the deliberate injection of a suitable gaseous tracer into a stream. The tracer is subsequently carried downstream and the rate at which it is lost to the atmosphere from the water is measured and expressed as a gas transfer coefficient, k . The rate of gas transfer that

exchange between the stream and the atmosphere is dictated by the gradient of gas concentrations across the air/water surface (Ellis et al., 1984). In stream experiments, the values of k for a soluble tracer can be related to the rate of oxygen uptake and expressed as a reabsorption coefficient (K_p). The gas transfer velocities of the two gases in a stream should be approximately the same because ^{86}Kr and SF_6 have approximately the same Schmidt number (Ellis et al., 1984).

CHAPTER 3 MATERIALS AND METHODS

Gas Chromatography and the Injection Port System

The gas chromatograph was the instrument used to analyze the SF_6 and the general procedures followed those of Marshall¹⁰ (1980). The entire chromatographic system consists of several pieces of equipment which have numerous components (Baker, 1983; Sullivan, 1987). The details for the entire system can be found in Appendix A. In general the SF_6 saturated water sample is fed into an injection port system that first separates the SF_6 gas from the carrier gas and sends both streams to the gas chromatograph to be analyzed. Once the SF_6 has reached the electron capture detector (ECD) within the gas chromatograph it passes through a beam of excited electrons (^{60}Co). Because SF_6 is a halogenated compound it has a high affinity for electrons and thus will disrupt the flow of electrons passing in front of its passage. This disruption in electron flow is translated into an electrical pulse which is read by the integrator. The integrator displays the time at which the SF_6 reached the ECD and an SF_6 area versus time curve. The area under this curve is compared to a previously

established standards curve and finally the concentration of SP_4 is calculated.

SP_4 Injection System

The injection system used to transport the SP_4 from its tank to the water consists of two major components. The details of the entire system can be found in Appendix B. These components are a 250L barrel and a two stage peristaltic pump. Basically, SP_4 is forced under its own pressure into a the water barrel. Once saturation is achieved, the water is then pumped via tygon tubing into the study region. The ends of the tygon tubing are held in place with two pound lead weights.

Thermometry

Thermometry is a simple tool that has been used to distinguish between ground water and surface water features. In numerous spider settings (Pitts et al., 1976; Larson et al., 1987; Coleman, 1988). To further distinguish between the Santa Fe River and water filled bareh features in the area, temperature readings were taken in many of the surface and stream water features. Locally, the ground water temperature remains at about 50-51°F year-round whereas surface water temperature varies depending upon local air temperature (Pearson and Patten, 1988). Temperature readings were taken on January 11, and 14, 1988, during the

coldest part of the year, to identify differences between surface features and ground water fed features. In March 1972 temperature readings were again taken to confirm these data. A thermometer, made of perforated metal, was lowered into the features to a depth of one meter until the temperature had reached equilibrium between the water and the thermometer. The thermometer was quickly removed and the temperature was recorded. This procedure was repeated three times at each location and an average temperature was then recorded. The precision of the technique was less than 0.2°C , determined by the 0.1°C divisions on the thermometer.

Sampling Techniques

SF_6 Sampling

For all mixing, flow measurement, water tracing and gas exchange experiments SF_6 was collected in either 50 ml biological oxygen demand (B.O.D.) prelabelled glass bottles or 10 ml glass syringes. For each sample, the bottle was conditioned once with the river or lake water and then the sample was drawn. Samples collected in the B.O.D. bottles were capped underneath the water to prevent air from entering the sample and thus allowing SF_6 to come out of solution. Samples collected in the glass syringes were filled to the 10 ml mark underneath the water and then any air found in the syringe was discharged at the surface. A volume of 10 ml was needed for each analysis.

Samples were stored on ice in a cooler and transported to the U.F. Hydrology Lab for analysis. The purpose for storing the samples on ice is to keep the SF_6 from coming out of solution at higher temperatures.

Rhodamine WT Sampling

Samples collected for the Rhodamine WT analysis were captured on activated charcoal packets following the procedure of May (1989). These pre-labelled packets consisted of about 4.18 grams of activated charcoal surrounded by a 18 cm long by 18 cm wide fine fiberglass sock attached to a wire connected and a weight. The wire was fastened to the weight so that when the charcoal packet was attached it would remain suspended above the floor of the river or creek (Figure 12). The packet was placed at the immediate opening of spring where possible to maximize rhodamine WT adsorption. This suspension of the packet also decreased the amount of debris that would become entangled on the packet thereby reducing the adsorbing capacity.

These samples remained in the water for 3.5 to 4 hours so that a definite rhodamine WT signal could be recorded (Pete Ross, personal communication, 1991). After collection, the sample was lightly rinsed with water, placed in a plastic bag, removed from sunlight and placed on ice until analyzed.

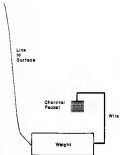


Figure 11. charcoal pocket used in surface HF gas tracing experiment.

The standard elution solution used was a mixture of 5% aqueous ammonia and 95% isopropyl alcohol solution. The isopropyl alcohol was 70% alcohol and 30% water. The aqueous ammonia solution was 5% ammonia. Twenty milliliters of the eluting solution was poured over the washed charcoal, capped and then allowed to stand for 40 minutes. The liquid was then carefully poured off the charcoal for analysis (Kley, 1970).

Radon Sampling

Radon water samples were collected in pre-labeled plastic 500 ml graduated cylinders specifically fitted for ^{222}Rn extraction (Figure 10). The pre-evacuated graduated cylinders were attached to tubes having fastened to a two inch diameter by three meter length of poly-vinyl chloride (pvc) tubing (Figure 11). This tubing was held at the desired depth, the inlet valve was opened and the water then flowed under pressure into the cylinder. A 100 to 500 ml sample was collected. The inlet valve was closed and then the cylinder was placed back into the water for later analysis.

Ammonia Sampling

Water samples for isotopic analysis were collected in pre-labeled 50 ml green glass bottles with screw on displacement caps. Each sample bottle was filled

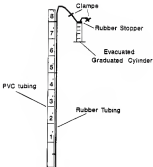


Figure 13. Sampling device and graduated cylinder for SF_6 and CO_2 .

conditioned, by rinsing the bottle with the river or sink water, and then collected at approximately 0.5 m depth in the water body. The cap was then secured while the bottle remained beneath the water surface.

Water Sampling

The major water sampling used glass (NOD) bottles. The bottles were cleaned following the procedures in Appendix C.

Quality Control

Duplicate samples were taken at intervals of about 14% of the total number of samples. In addition, duplicate analysis of the same sample were performed at 14% intervals of the total number of samples taken. Duplicate analysis of the same sample were impossible because the total volume of each sample was needed in the analysis for the gas chromatograph (H_2S), the fluorometer (rhodamine WT) and the redox extraction system H^+As . However, duplicate sampling was executed whenever the number of sample containers allowed.

Injection Methods

During the Summer of 1991, two twelve-hour long retention experiments were carried out on the North Fo River which required the continuous injection of H_2S over a

certain time period. A two-channel peristaltic pump was used to inject 200 liters of SF_6 saturated stream water at two points across the river at a rate of 10L/minute. The governing constraint, in determining the length of reach used in each of the experiments, was the time required for SF_6 to reach plateau concentrations in the stream. It took about five hours for plateau concentrations to be reached in the Santa Fe River (Figure 13).

Heavy sampling over the entire length was carried out after plateau concentrations were reached. From fifty to 100m downstream of the injection point, samples were collected based on predictive equations and the results of the mixing study (Potter et al., 1984). Lateral and vertical mixing problems in the river channel were minimized by collecting integrated samples 1/3 depth of the stream by direct suction into bottles. In addition, SF_6 grab samples were also collected at two points across the stream in the second reconnaissance study. Immediately following the experiments both ^{222}Rn and SF_6 samples were analyzed on a 24 hour schedule. The margin of error for sample analyses was calculated by analyzing river water samples during plateau levels at three positions. The SF_6 concentrations were within an average of 7% of each other.

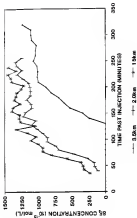


Figure 17. Plot to platform for SF_6 in the tanks in the river.

Analytical Techniques

Gas Chromatography

Gas chromatography is a physical method of separation, in which the components to be separated are distributed between two phases. One of these phases constitutes a stationary bed of large surface area (the column packing material), the other being a fluid that percolated through the stationary bed (the carrier gas and sample gas) (Paulsson, 1977; Kaiser, 1984).

In the case of SF_6 analysis, a sample was injected into the separating column filled with a micro-sieve mesh, with ultra high pure (999+) grade nitrogen gas. The carrier gas, nitrogen, and SF_6 were then separated and sent to the gas chromatograph where each was analysed with an electron capture detector (ECD). The ECD is a device that basically consists of cathode as source and a recording device. The radioactive ^{63}Ni emits electrons (beta particles) across a nitrogen carrier stream onto an anode. There a recording device records the resistivity of the passing electrons. If the stream is interrupted by a substance absorbing electrons, like SO_2 , the output signal will change. Interpretation of this analysis is then recorded by an integrator which graphically and quantitatively indicates the presence of SF_6 in each sample. This method is highly sensitive, rapid and simple in execution. Accurate,

quantitative information can be obtained using small amounts of sample (Bévil).

Fluorometer Procedure

A fluorometer's method of detection is completed by interpreting a sample's amount of light reflectance. A sample is quickly passed through a port that continuously reads the light reflectance property of the fluid. In order for a fluorometer to accurately read a sample it must remain in the sample loop for at least 15 seconds (Riley, 1994). Some Turner Design Model 10 Fluorometers can be modified to analyze the standard three milliliter sample that is typically used in lab fluorometers. The fluorometer used in this study was not modified because of lack of funding to complete the process. Because the sample taken was the same volume as the sample loop, the continuous running of the fluorometer passed the sample very quickly through the sample loop and therefore did not allow sufficient time to quantitatively determine the sample's rhodamine concentration. However, relative measurements of the strength of the solution passing through the loop could be determined by recording the degree to which the fluorometer's needle was deflected. Values such as strong (4), moderate (3), weak (2), very weak (1) and none (0) were recorded for each of the samples.

Radon Analysis

^{222}Rn was stripped from water using a small extraction system and transferred to an airtight chamber. The radioactive disintegrations of the ^{222}Rn trapped in the chamber, a modified Lucas-type scintillation cell, were measured and recorded by an alpha-scintillation counter. The scintillation counting material is mounted on the face of a photomultiplier tube, the pulse of light produced by the radiation is converted to an electrical pulse which in turn may be amplified and counted. For work with short range, densely ionizing radiations like alpha particles, the scintillator is finely crystalline zinc sulfide coated in a thin layer on the face of the photomultiplier. The technique and analytical equipment are fully described in Elliot (1968).

The error reported for the radon analysis is a composite of the errors associated with sample counting, cell background counting, channel noise, volume, cell efficiency, and operator error. The precision of the entire procedure was determined by running duplicates of 11 samples in the lab. The level of uncertainty associated with precision of the method does not exceed 10% (Elliot, 1968).

Radon Absorption Spectrometry

Two water samples were taken at 0.3 m depth, in B.O.B. glass bottles previously cleaned in nitric acid and triple

distilled water from 10 locations throughout the park. Water samples from the adjacent Santa Fe River were also analyzed for major cation chemistry. The samples were then analyzed for the major cations Ca^{2+} , Mg^{2+} , Al^{3+} , K^+ , and Na^+ on a Perkin-Elmer model 1100 atomic absorption spectrometer using the acetylene flame ionization techniques outlined in the Perkin Elmer manual (Perkin Elmer, 1980).

The basic technique involves developing a standard curve using lab standards for each of the elements being analyzed and then analyzing samples which fall along the standard curve. In concept the sample is ionized by an acetylene flame in the presence of a light beam emitting the frequency of absorbance for the element in question. Once the sample has been ionized the amount of absorption of this light is recorded. This absorption is then compared to the standard and statistically plotted along the standard curve which calculates its actual concentration. In the University of Florida lab, software that accompanies the spectrometer automatically calculates the concentration of cation within the sample. Each sample was analyzed twice and an average value was recorded.

Conceptual Modeling

A model is a tool designed to represent a simplified version of reality. In general, mathematical models use governing equations limited by boundary conditions to

simulate the flow of ground water (Luckner and Robertson, 1981). Using calculus, it is sometimes possible to calculate the heads at given points as a function of space coordinates and thus generate an analytical solution. To obtain this solution several simplifying assumptions about the aquifer must be made, including: 1) homogeneous stratigraphy, 2) isotropic conditions, 3) a linear water table configuration, and 4) approximation of the problem by a rectangle (Wang and Anderson, 1982).

For many modeling problems these assumptions are unrealistic and require use of numerical methods to solve the mathematical model. Governing equations are approximated by algebraic statements, boundary conditions, and by programming techniques. Finite difference models are based on rectangular grids whereas finite element models use grids made of triangular elements. Iterative calculations produce estimates of hydraulic head at nodal points that eventually converge to values of acceptable accuracy. Models are calibrated by matching computer-generated head values with field measured head values within reasonable limits (Mercer and Hunt, 1981).

Numerical Models

Finite-difference methods used to solve partial differential equations use a grid of rectangular cells to represent the region of interest. For two-dimensional

problem a grid system is overlain on a map view or cross-section of the aquifer (Hantush and Fract, 1963). At each grid node the head will be calculated based on equation in

$$(8)$$

$$\Delta x \Delta y (T_x \partial^2 h / \partial x^2) + \Delta x \Delta y (T_y \partial^2 h / \partial y^2) + S \partial h / \partial t = Q(x, y, t)$$

where

$$T = transmissivity, L^2 T^{-1},$$

$$h = \text{head, } L,$$

$$t = \text{time, } T,$$

$$S = \text{storativity,}$$

$$Q = \text{net ground water withdrawal, } L^3 T^{-1},$$

$$x, y = \text{rectilinear coordinates,}$$

for which there is no general solution. but through the finite-difference approximation a numerical solution can be obtained by replacing the derivatives in equation 1 by differences taken between nodal points (Hantush and Anderson, 1963). At each finite-difference node the form of equation 1 at node (i, j) in equation is

$$(9)$$

$$T_{i+1,j} (h_{i+1,j} - h_{i,j}) / \Delta x^2 + T_{i,j+1} (h_{i,j+1} - h_{i,j}) / \Delta y^2 + \\ T_{i,j} (h_{i,j+1} - h_{i,j}) / \Delta y^2 + T_{i,j} (h_{i,j-1} - h_{i,j}) / \Delta y^2 = \\ + (h_{i,j} - h_{i,j-1}) / \Delta t = Q_{i,j} / \Delta x \Delta y,$$

where

$h_{i,j}$ = the calculated head at the end of the previous time increment, t_i

$T_{i+1,j}$ and $T_{i,j+1}$ = aquifer transmissivity within

the vector values between node i,j and $i+1,j$ ($i+1,j$: $i,j+1$; $i,j+1$: $i,j+2$) (Figure 14).

Because nodes throughout the entire grid have equations in the same form as equation 3, these equations are solved simultaneously for the unknown h_{ij} variable (Lockner and Schmalzer, 1991). By allowing ∇ (anisotropy) to vary with time as the thickness of the aquifer varies, equation 3 can be used in unconfined cases (Wang and Anderson, 1982).

A model based upon the two-dimensional FIASM (Fractured and Isotropic Aquifer Simulation Model) and MOD (method of characteristics) program was used to simulate ground water flow conditions around the O'Leary State Park and western Santa Fe River region (Lockner and Schmalzer, 1991). These models were chosen because their computer requirements corresponded to the facilities available. Also, they were accessible and relatively powerful with respect to the kinds of data needed as input.

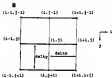
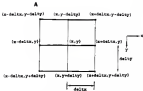


Figure 14: Computer modeling coordinates. A. Finite difference grid. B. Computer notation for finite difference grid (after SWEET, 1982).

CHAPTER 4
RESULTS AND DISCUSSION
Mixing Experiments

Introduction

The management of mixing characteristics, longitudinal and transverse dispersion, has been studied in detail in order to address the stream capacity of handling pollution and to determine alternative loading techniques and tracer types. Previous procedures have employed saline solutions, rhodamine dyes, ethylene, propane and reflective tracers to measure these mixing attributes (Lutz et al., 1980; Johnson and Nathan, 1982; Kocumore et al., 1978). Mathematical models have been derived to calculate the concentrations of a tracer under certain stream conditions over time and distance to understand mixing processes (Fleisher, 1966; O'Loughlin and Brown, 1975). However, these models have often made several assumptions about stream parameters (i.e. bed roughness, velocity parameter, channel degradation and diffusion). By making these assumptions they allow for greater error in their predictions. More importantly the models do not readily offer the flexibility of additional sources and sinks for river water and or ground water in

complicated riverine conditions which can greatly affect the stream's mixing capabilities.

In the baroque terraces of the western Santa Fe River basin assessing mixing parameters of the stream is made difficult by the numerous springs, seeps, siphons and boils found within the Santa Fe River. In order to accurately obtain a representative sample of river water for analysis, these detailed mixing experiments were devised to address the cross sectional distribution in the variable dissolved gases, natural radon-222 (^{222}Rn) and artificial surface benzotrifluoride (BF_3).

Radon-222

The use of radon-222 (^{222}Rn) in monitoring the relationship between ground water and surface water has been employed in a variety of hydrologic and geologic ground water settings (Boggs, 1958; Branstetter et al., 1967; Jacoby et al., 1970; Hunsinger and Moore, 1968; Elliot 1969, 1969; 1968; 1969; Lee and Reddy, 1967). Although these authors have described the concentrations of ^{222}Rn throughout a reach of a river they neglect to address the lateral and vertical variations of radon concentrations throughout the water column which may be significant.

Because ^{222}Rn is inert, naturally occurring, reaches equilibrium with the host aquifer within a short time period (about one month), and is often found in a much higher

concentration in ground water versus surface water and remains in solution in the aquifer until the ground water is discharged, it can be used to identify pulses of ground water to many surface features. This process has been described in Gillis and others (1988).

Sulfur Hexafluoride

SF_6 has been used in the medical field as a dense displacement gas, in atmospheric tracer experiments, ocean circulation experiments, to monitor gas exchange in lakes and rivers and as a ground water tracer (Lovelock and Ferber, 1980; Ledwell, 1984; 1988; Ledwell et al., 1986; Ledwell and Watson, 1988; Wassenaar et al., 1987; Wassenaar et al., 1988; Elvert and Gillis, 1989).

The artificial tracer, sulfur hexafluoride, (SF_6) was selected for this study over other tracers propane, ethylene and rhodamine WT because it is inert, non-biodegradable, nontoxic and can be detected in extremely low concentrations (femtograms per liter). Also, it does not have some of the associated problems that rhodamine WT has with organic acids that are commonly found throughout many southeastern U.S. states, including Florida (Fernald and Fether, 1984). The major problem of using rhodamine in Florida streams is that the naturally tannin streams create a high background fluorescence, thus making rhodamine identification difficult. In addition, SF_6 is relatively inexpensive

compared to rhodamine and samples can be analyzed quickly, approximately 15 samples per hour, following the procedures of Wenzelbach (1986). As part of this study the refinement of injection and sampling procedures for riverine environments was also completed.

Processes of Dilution and Mixing

When solute material is injected into a flowing stream, its eventual fate is determined by the physical process of diffusion, convection, chemical degradation, adsorption and evaporation. If a tracer is injected at a point in a flowing channel, it is immediately subjected to the process of turbulent diffusion and dispersion, and its concentration tends to become uniform in the cross-section (O'Loughlin and Bower, 1975; Flute and Friedrich, 1984). The distance required for near uniformity to be achieved may typically be on the order of hundreds of times the channel width (O'Loughlin and Bower, 1975). The events in this stage are three-dimensional and the actual spread rate of dilution depends on the channel geometry and the large-scale turbulence structure of the flow. At this point in the evolution of mixing and dispersion theory, it is difficult to predict the length of this initial phase (O'Loughlin and Bower, 1975). However, it does appear that the mixing length is determined by the same physical parameters which determine the later dispersion phase in the dilution of the

tracer. Attempts to characterize the behavior of the tracer in the initial stage by using one-dimensional formulations are suspect and lead to erroneous predictions of tracer attenuation.

During the dispersion phase, the tracer behaves as a one-dimensional slug of material in the channel; the only significant concentration gradient is that in the direction of flow. A more detailed description of the mathematical derivation of the one-dimensional dispersion equation can be found in O'Loughlin and Power (1975). Concentrations for a given time period can be predicted for a non-conservative tracer using the following equation:

(8)

$$c(x,t) = \frac{M}{(4\pi D t)^{1/2}} \exp(-Et) \exp\left[-\frac{(x-ULt)^2}{4Dt}\right]$$

where

- U = mean velocity, m/s
- D = longitudinal dispersion coefficient,
- E = first order decay constant for the tracer,
- x = distance, m, and
- t = time, s. (O'Loughlin and Power, 1975).

According to Gred (1966) the distance needed in order to achieve complete transverse mixing within a stream can be calculated using the equation:

(9)

$$L = \frac{0.17 \, W^2}{E}$$

where

V = mean reach velocity, m/s

B = stream width, m

K_m = transverse mixing coefficient (equal to $0.4Vd$), where:

d = dimensionless constant, 0.2 for straight streams 2.5-5.0 for more irregular stream sides and bottoms,

d = mean depth, m.

u = shear velocity, m/s.

Using this equation, estimates of length of mixing for three reaches of the Santa Fe were calculated. Because of the uniformity of slope and discharge along the river reaches sampled, the average length of stream needed for complete mixing was calculated to be 1.4 km. This estimate was tested in an earlier experiment on the Santa Fe and revealed a complete mixing between 1.5 and 1.8 km, as the equation had predicted.

Because of the river's complex hydrologic character, four separate mixing experiments over three different reaches of the Santa Fe River were completed.

Injection at Wilson Springs

The initial injection experiment took place on June 9, 1961 between Wilson Springs and 2.0 km downstream of Wilson Springs. This site was chosen because of its relative ease of access to the Santa Fe River and its close proximity to our working base camp (Figure 18).

The goals of this experiment included 1) determination of the average stream velocity, 2) testing the SP_1

injection design, 3) determination the river's lateral mixing component, the length at which an injected tracer would become completely laterally mixed, 4) testing the sampling strategy, 5) testing the analytical procedures and equipment with field drawn samples.

Experiment Design

Samples were obtained at four sites located 2.5 km apart and at the SP_1 injection site, which was located approximately 18 m downstream of the Wilson Springs heat ramp. Samples were collected from a stationary canoe at a depth of 0.3 m in BOD (biological oxygen demand) bottles. In some instances, 50 ml glass syringes equipped with three-way tips were used instead of the BOD bottles, but the general sampling strategy was the same. The sample was taken and capped at depth. The bottle was then transferred to the shore and stored until analysis took place. A predetermined time at which to start the sampling and the SP_1 injection was relayed to the volunteers before they were stationed at their sampling points.

Hollingsworth Bluff

The second experiment was carried out at Hollingsworth Bluff. This site was chosen because no known springs or fissures have been identified in the area, it is relatively straight and has a constant depth and width, and thus ¹³³Xe

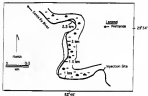


Figure 18. Lower Santa Fe River near Wilson Springs (from Kilian et al., 1983).

was assumed to be being well mixed in this reach (Figure 18). In addition, because the reach is relatively straight a uniform velocity profile can be assumed. Three cross sections spaced 100 meters apart were sampled for ^{222}Rn . Twenty samples were taken at each of the locations labeled Mix 1, Mix 2 and Mix 3 on Figure 18. Four water samples were collected at equally spaced intervals across the width and depth of the stream. Water samples were collected via rubber tubing assumed to 5 cm PVC piping, previously marked in 0.5 meter intervals, with an open end in the water and the other end attached to a previously evacuated 100 ml graduated cylinder. The graduated cylinder was opened once the tubing reached the appropriate depth and the vacuum created within the cylinder sucked water up from depth filling the graduated cylinder to about 100 ml. Samples were then stored in a cooler and then taken back to the lab to be analyzed. In addition, two integrated samples were taken, one across the width of the stream at 0.5 meters depth and the second taken vertically mid-stream throughout the top three meters of the water column.

Six stream velocity measurements were also taken at each of the three locations using a Wetzel-Stanton Flow Meter, to monitor the total discharge over the sampling area. ^{222}Rn measurements were made using Lucas-type scintillation cells with alpha scintillation counters. A small portable extraction system was used to strip the ^{222}Rn



Figure 11. Sample locations at Hollingsworth Road (from Gilson et al., 1992).

from water samples collected in the field into minimization cells.

River Mile to Two Kilometers

The third experiment evaluated the mixing characteristics from the River Mile of the Santa Fe River to 2 km downstream using a continuous injection of SP_4 from a point source located in the middle of the river (Figure 17). This reach was investigated to examine the effects of the known holes located within the river between 0 and 0.45 km and 0.75 and 1.0 km. SP_4 was continuously injected into the river until plateau levels were reached, approximately two hours. About twenty water samples were taken across the width of the three locations, at 0.5, 1.0, and 1.5 km downstream of the River Mile, using a similar method to that employed in the first mixing experiment. Subsequent sampling locations at 2.0, 2.5 and 3.0 km were sampled but samples became unusable after transportation because they became aerated as they were sampled incorrectly. Discharge measurements were taken before and after the samples were taken to ensure constant river flow.

Two Kilometers to Spring Springs

The fourth mixing experiment was carried out in an area characterized by several springs and river oxbows approximately 10.75 km downstream of the River Mile, near

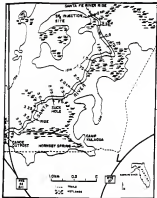


Figure 17. River flow to four kilometers on lower Santa Fe River (from Collins et al., 1993).

Minde Springs (Figure 18). Sulfur hexafluoride was injected near Hot Island Spring in the middle of the river through a single point source. Water samples were taken at three points across the width of the stream at 0.5 m depth at 13 locations downstream of Hot Island. Between 15.5 km to 16.75 km water samples were taken every 150 m and from 16.50 km to 17.50 km, every 50 m. Sample spacing was altered in this area in order to evaluate an experiment that was being carried out beneath the river, within the Devil's Ear flow system, in conjunction with the SF₆ mixing experiment. Discharge measurements were taken at four locations throughout the length of the experiment.

Summary of Mixing Experiments

Wilson Springs

Stated goals of the mixing experiment were accomplished. The lateral mixing component was described in this experiment. Using equation 5, the distance needed for complete lateral mixing was calculated to be 1.4 Kilometers under the flow conditions of the experiment. This value also agrees well with the concentration response curves found in Figures 18 and 19. A concentration response curve that shows a typical rising and falling peak with one central peak describes a location where there is complete lateral mixing. At 0.5 km the mixing is incomplete due to

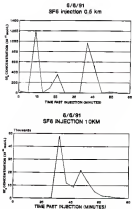
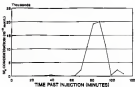


Figure 18. SF_6 concentration response curves 0.5 to 1.0 km.

8/6/91
SF₆ INJECTION 1.5KM

88



8/6/91
SF₆ INJECTION 2.0KM

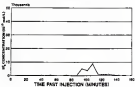


Figure 28. SF₆ concentration response curves 1.5 to 2.0 km.

the multiple peaks and random distribution of SP_1 throughout the sample period of 30 minutes. At 1.0 km mixing is not yet complete as two peaks are easily recognizable at this local. At 1.5 km mixing is complete as indicated by a rising and falling curve with one central peak.

The velocity of the river was also calculated using the centroid of area of the tracer curve. Using the concentration response curves at locations 1.5 and 2.0 km (Figure 20), the velocity calculated over these two distances was 0.275 m/s and 0.303 m/s, respectively. These values corresponded well with velocity measurements taken with a Weatherstream flow meter which revealed average stream velocities of 0.275 m/s at 1.5 km and 0.285 m/s at 2.0 km.

This experiment established a reliable, field worthy injection system, used repeatedly over the last threeyears without any major changes. The system described in Appendix A was used with only minor adjustments throughout this and all other SP_1 injections described in this dissertation. Secondly, the sampling design using Bob bottles and glass syringes in conjunction with canoes and coolers to store samples in ice was also effective. Sampling times and intervals based upon equation eight accurately captured the rising and falling edges of the tracer as it made its way downstream. Thirdly, the analytical techniques and gas chromatograph system described in Appendix A was also

productive in analyzing SF_6 samples efficiently, expensively and with a high degree of precision.

Ballingworth Cliff

Table 3 provides the ^{222}Rn statistical data calculated for the three stream cross sections sampled. At 100 m the concentrations vary the most across the width and depth of the river, from 40 dpm/L found along the stream bottom, to 110 dpm/L recorded in the middle of the stream. The three cross sections in Figure 11 show the contoured distribution of ^{222}Rn concentrations at 100, 200 and 300 meters from the reference point at Ballingworth Cliff.

Below-100 values recorded at 100 meters ranged from 115 dpm/L to 164 dpm/L. Variability in ^{222}Rn values diminished with distance downstream of the injection point. At 300 meters all values appeared to increase over the 100 m distance and the variability between sample locations decreased to its lowest level. The increase in concentration is probably due to a diffuse influx of ground water between the last sampling site and 100 m and its dispersion throughout the water column. The standard deviation suggests that all values fall within 15% of the average, the precision of the reference analysis. The contoured data also reflects this homogeneous trend.

Horizontal and vertical samples taken across the width of the stream at 0.5 meters depth and at midstream from

Table 5. Statistical data from mixing experiment #2, ^{222}Rn data reported in dpm/l.

Parameter	100 m	150 m	200 m
Average of all samples	143	153	189
Standard Deviation	58	67	36
Number of samples	20	20	10
Horizontal Sample	140	149	174
Vertical Sample	145	176	160
High	151	166	186
Low	81	121	170

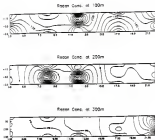


Figure B1. Contoured cross-sections of ^{226}Ra concentrations in the river near Ballingworth Kraft, distances are in meters, contour interval equals 10 dpm/l.

better to try reveal close approximations to the overall average of all samples taken for the stream cross section. In most cases both integrated sampling methods were within approximately 10% of the stream average. Because the horizontal and vertical samples reflect an overall stream average it is suggested that this type of sampling procedure be followed when sampling a stream that has springs feeding the main river channel.

River Rise in Ten Kilometers

Trifluoromethane was sampled at 10-20 locations within each of the three cross-sections at 0.5, 1.0, and 1.5 km using the same techniques of injection, sampling and analysis as in the first mixing experiment at Wilson Springs. A well-defined pattern was recorded beyond the 1.5 km distance from the injection point.

the CF_3 concentrations were lower than expected (Figure 20). In each of the three sample locations CF_3 concentrations were about an order of magnitude lower than previous experiments and the third mixing experiment. This is probably due to the continuous influx of unenriched non- CF_3 enriched water to the river system throughout the upper reaches, between 0 and 100 m and between 700 m and 1000 m coming from holes and seeps in the river. In addition, the holes in the river further escape the water which causes the water to lose CF_3 faster to the atmosphere than a stream

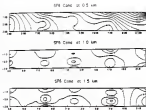


Figure 19. Mining results at 0.5, 1.0, and 1.5 km downstream of the River Elm, dimensions are in meters, contour interval varies.

without this boiling feature (penetrated, 1944). The results of this study are useless due to their values being close to the detection limit of the procedure.

San Isidro to Abasco Stream

In this relatively straight reach of the river covering about 1.5 km, 15 SF_6 samples were collected after plume levels of SF_6 were reached in the stream about 2.5 hours at three equally spaced locations stretched across the width of the Santa Fe River. Figure 21 shows the contourd SF_6 concentrations and locations of major springs along this reach. The continuous input of Blue Springs water greatly depresses the plume of SF_6 as it moves in a downstream direction. Along the southern bank of the river, Blue Spring which discharges greater than $1.15 \times 10^3 \text{ m}^3/\text{y}$ of water keeps the SF_6 from thoroughly mixing throughout the 1.5 km reach of the river, and its effect creates a plume-like wedge of ground water into the Santa Fe River.

Discussion

The application of SF_6 allowed for the characterization of stream parameters such as velocity, mixing (lateral, vertical and horizontal), and spring influence on the distribution of river dissolved gases. That is, by injecting SF_6 into a streamine environment with known spring influence, the effect of these springs on the dispersion of

water within the stream water column can now be assessed. In addition, the injection of SF_6 into a region with no prior knowledge of springs or seeps may also indicate the location of such features.

Field methods including equipment, injection setup, water sampling and analytical methods for SF_6 have also been established. This work provides the foundation for future riverine experiments employing SF_6 as the water tracer. Moreover, naturally occurring ^{222}Rn can also be used to interpret spring locations and mixing characteristics throughout a stream cross section. The distribution of ^{222}Rn gas throughout a cross-section of the Santa Fe River is dependent on several variables, dispersion, stream roughness, stream depth, stream velocity, stream profile, and the location of the ground water source (Fetters et al., 1984). These experiments show that in this karstic setting, concentrations of ^{222}Rn decreased with depth and appear to be dependent upon source area.

The overall average cross section concentrations correlate well to both the vertical and horizontal sampler tubes at the midpoint of the stream. On the basis of these experiments, future river water sampling should be done in an integrated fashion to account for concentration variations that may exist in the stream cross section, even though complete mixing is assumed in the reach of the river.

Water Tracing Experiments

O'Leary Sink To River Rise

At the request of O'Leary State Park managers, a gaseous tracer experiment was conducted during July 1991. This request came forth because a rapidly opening sink hole "New sink" had opened apparently overnight within O'Leary State Park boundaries. Their purpose was to determine the relationships among the Santa Fe River, surface water and sink holes along the five kilometers underground portion of the Santa Fe River within O'Leary State Park, Columbia County, Florida.

A gaseous tracer, SF_6 , was introduced into O'Leary Sink for two hours. After this injection, seven sinks between O'Leary Sink and the resurgence of the Santa Fe River were monitored over a four to 16 hour period to determine ground water flow paths and traced times and duration of the gaseous tracer within the sinks and the River Rise.

O'Leary State Park is located on the borders of Columbia and Alachua Counties in north central Florida (Figure 24). Within the park, the Santa Fe River flows southward and is diverted underground for approximately five kilometers. The Santa Fe River rises and continues to flow in a westward direction.

Within the park there are numerous karstic features: sink holes, water filled sinks, springs, and water filled

features. The features range in size from a few meters across to two or three kilometers in length. It has been observed that some of the features have flowing water, (New Sink), while others appear to be stagnant (Two Mile). In addition, some features have clear water similar to that of "pure ground water" while others contain the typical brown stained, dark waters of the Santa Fe River and surrounding wetlands.

Initial reconnaissance of the O'Leary State Park began in early July, 1981. Topographic and park maps along with aerial photos were interpreted to determine possible connections between sinks in the park. A tracer experiment was designed to determine the connections and travel times between O'Leary Sink, several sinks within the park and the River Mile.

Sinks were chosen based on four criteria: 1) visual observations of water movement through the sink, 2) accessibility, and 3) potential connection to underground and 4) lack of alligators.

Discharge measurements and bathymetric surveys of O'Leary Sink and the River Mile were completed. Discharge measurements were needed to get a rough estimate of the amount of water flowing through the region in order to determine the injection rate of the tracer. The bathymetric surveys at O'Leary Sink and the River Mile were carried out

to locate the best depth for injecting the tracer and sampling for the tracer.

The injection system was set up over O'Leary Sink following these measurements. Twine was strung above the sink and centered over the deepest area within the sink so that floating debris would not entangle the injection tubing. The air injection system used in the previous experiments was set above the eastern edge of the sink. Injection of the river water was completed using a peristaltic pump and two lengths of tygon tubing as previously described in the Wilson Springs experiment. The injection tubing extending out from the drum was placed over the center of the sink. Two injection points, one midway in depth (about 150) and the second at the bottom of the sink (about 180) were put in place to assure that the tracer would enter the conduit system.

Injection of the tracer occurred over a two hour time period so that an adequate sampling window would be available downstream of the injection site. Sampling the sink and river area was limited by three 1) number of volunteers, 2) number of sample containers, 3) number of sinks sampled, 4) sampling interval, and 5) total sample time.

Where possible one end of the sink was designated the "sampling end" based on the observation of flow coming up from depth creating a boiling appearance at the surface.

Where this feature was not visible a sample was simply collected from a gauge from the middle of the sink. Samples were collected as a grab sample of water at some depth (about 0.5m) in a glass 5.0 L bottle or glass syringe. After collection, the samples were stored in coolers filled with iced water and then transported back to the University of Florida for gas chromatographic analysis.

Initial minimum estimates of tracer travel time from the injection site to individual sinks were determined using the discharge measurements determined at O'Leary Sink and straight line distances between sinks (equation 4):

(4)

$$t_L = 5.48 + Q^{-1.0} + X^{1.0}$$

where

t_L = travel time to leading edge of tracer
 Q = discharge, m³/sec
 X = distance downstream of injection, m
 (from Nathan, 1979).

The maximum time allowed for sampling for a two hour injection was determined using equation 5.

(5)

$$P = 1.41 + T^{0.75}$$

where

P = passage time for tracer "cloud"
 T = travel time estimated from previous calculations, peak travel times
 (from Nathan, 1979).

SINKS

Eight sinks (Oxley Pond, Levine Sink, Burners Branch Sink, Small Sink, New Sink, Jim's Sink, Two Hole and

Swanwater Lake) and the River Rise were sampled over a four to 16 hour period depending on the location along the rivers interpreted underground path.

An average discharge of $44\text{m}^3/\text{s}$ was recorded above O'Leary Sink two days prior to the injection of tracer. Bathymetric surveys of O'Leary sink revealed that the deepest part of the sink was located along the eastern edge of the sink (Figure 18). Its maximum depth was approximately 14 meters, confined to two points along this edge. The sink was much shallower, maximum depth 14.3 meters, and broader along its banks (Figure 19).

It was determined that a relatively unknown amount of water may be entering the underground system at any time. Also, several conduits may be taking the tracer downstream, dividing and then recombining the mass and diffusing waters further diluting the tracer. In addition, exposure of the tracer to the atmosphere would also cause a loss in SF_6 concentration. Based on these assumptions the tracer was injected at the pump's maximum rate, approximately 110 liters per hour. Based on initial travel time estimates and total passage time of the tracer cloud, it was determined that a two hour injection would be sufficient to sample downstream sinks. After the completion of this slow injection the remaining contents of the barrel were dumped into the sink to see if it could be detected as a spike in the downstream sinks.

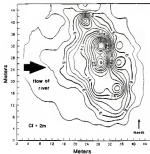


Figure 18. Bathymetry of O'Shea Sink.

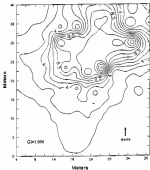


Figure 28. Bathythermy of River Nile.

Utilizing as many samples as possible within the shortest sampling interval, about 200 samples were taken over the 12 hour time period at eight locations. Minimum travel times were calculated using equation 4 (Table 4). Passage times for the tracer alone are more difficult to determine because mathematical equations predicting these times do not take into account residence time of the tracer within the sink itself. However, they can be used to give a minimum estimate of the sampling volume at each sink. Using equation 7 estimates of passage times were determined (Table 5). Note that T here is not the time calculated in the first equation but rather a time calculated as the travel time of peak concentration.

Salifer bauxite was detected in all but one of the locations, River Mile. In all but one of these locations, Two Mile, the initial peak was detected to within about a half-hour time period.

The concentration response curves for Gypsum Pond, Spring Sink, Ferguson's Branch, Small Sink, New Sink Flie's Sink and Duckwater Lake are shown in Figures 17 and 18. Table 4 provides the arrival times for the leading edge of the tracer (T_0), the travel time of the centroid of 40% (T_0), and the total tracer passage time for those sinks monitored for a sufficiently long interval. The mid-point of the two hour injection (one hour) was used to calculate the centroid of the mass (T_0), except for 40% clay injection which was

Table 4. Estimated time until landing edge of tracer reaches sink.

Location	Minimum	Travel Time	
	Distance(km)	Hours	Minutes
Opdam	0.1	0.01	0.7
Narvik	0.7	0.04	2.7
Permanua	0.95	0.04	34.5
Sæli	1.0	0.24	15.0
See	1.1	0.29	17.7
Jile'n	1.2	0.35	19.5
Two Mile	1.5	0.45	26.8
Sawtooth	2.0	1.03	33.1
River Mile	4.75	1.64	121.9

Table 5. Estimated passage time for the tracer cloud at each sink.

Location	Minimum	T	Passage Time for
	Distance(km)	Seconds	3 hr. Inject. (min)
Opdam	0.1	0.00	188
Narvik	0.7	0.04	189
Permanua	0.95	0.04	188
Sæli	1.0	0.24	188
See	1.1	0.40	190
Jile'n	1.2	0.44	196
Two Mile	1.5	0.75	207
Sawtooth	2.0	1.11	211
River Mile	4.75	1.97	259

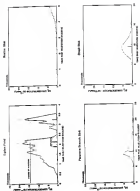


Figure 17. Concentration response curves for Optics field, Surface field, Infrared field and Small field.

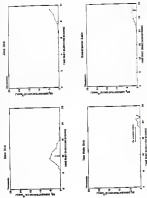


Figure 18. Concentration response curves for two plates, one's slide, two holes and two holes and one's slide.

Table 4. Travel times for SF_6 at sinks in O'Leary State Park.

Site	Distance from O'Leary Sink (m)	Distance			T (min)	Avg. Vel. (m/hr)
		T_0 (min)	T_p (min)	Percentage (%)		
Ogden	160	14	125	100	54	0.84
Service	487	181	*	*	*	*
Parsons	1323	160	558	480	488	0.84
Small	1474	184	588	434	518	0.84
New	1821	104	608	443	528	0.84
Jim's	1781	480	*	*	*	*
Two Mile	3257	480	*	*	*	*
Quatre.	4341	478	1147	*	1088	0.84
Time	6021	**	**	**		
Ogden (SF_6)	160	14	73	14	73	0.85

* period of sampling was too short, ** no SF_6 was detected.
 T_0 = time to leading edge of tracer, T_p = time to peak concentration, T = travel time of centroid of the SF_6 mass.
 T, travel times were calculated from the mid-point of the two hour injection (3 hour), except in the case of the response curve for the SF_6 slug injection, which would only be monitored at Ogden Pond. As distance from the injection site at O'Leary Sink increases, the two response curves merge due to dispersive mixing and the result is a single broad response curve at Small Sink, New Sink and Quatrevier Lake. Estimated mean underground flow velocity between O'Leary Sink and Fourmile Lake is 4.3 km/day.

be monitored at Ogden Pond. In this case, CF_4 was calculated from the point in time when the CF_4 emission remaining in the barrel was dumped into Ogden Pond. Table 4 also provides the average travel velocities calculated using the centroid of mass travel times and the straight line distance between the sinks. Using these data, an average unsaturated flow velocity of 4.3 km/day between Ogden Pond and Sweetwater Lake was determined for July, 1980, a period of unusually high flow ($400 m^3/s$, during July 1980 versus $150 m^3/s$ normal; Mann and Black, 1983).

The entire passage of the tracer cloud was recorded at four of the eight sampling locations Ogden Pond, Farmer's Branch Sink, Small Sink, and New Sink. Sampling did not occur long enough at Ravine Sink nor the three most distant sinks from the injection point (Jim's Sink, Two Hole and Sweetwater Lake). During 18 hours of monitoring, CF_4 was not detected at the Santa Fe River Sink. One possible explanation for not detecting any CF_4 is that the duration of the sampling period required to monitor the tracer was underestimated and sampling was stopped before the leading edge of the CF_4 front arrived at the Santa Fe River Sink. Another possibility is that the tracer masses diluted by ground water, added along the flow path, so that the concentrations were too low to detect. Another possibility is that the River Sink was not the primary resurgence of the underground Santa Fe River.

A significant decrease of about 50% in SF_6 concentration noted between Elm's Sink and Fox Hole Sink raised the possibility of greater dilution by mixing with ground water. Discharge measurements obtained during the experiment, however, did not reflect a gain but rather a loss of about $4 \text{ m}^3/\text{s}$ between O'Leary Sink ($21.3 \text{ m}^3/\text{s}$) and the River Sink ($17.4 \text{ m}^3/\text{s}$).

Swanwater To Santa Fe River Sink

Because SF_6 was not detected at the River Sink in the first tracing experiment, a subsequent study was carried out between the point of last SF_6 detection, Swanwater Lake and River Sink. In this experiment SF_6 was injected into Swanwater Lake in the downstream end of the sink. The injection process was the same as the one used in the O'Leary Sink injection with a two hour injection period of 814 L of SF_6 saturated, Swanwater Lake water. A sampling schedule based on equations ten and eleven was also produced for the three downstream locations at the River Sink, and 10 m and 100 m downstream of the River Sink. In addition, ground water travel velocities were also estimated based upon the earlier tracing experiment, which further determined when sampling was to begin and end for this experiment.

In this trace, SF_6 was detected at River Sink providing evidence of a link between Swanwater Lake and River Sink. Since the connection between O'Leary Sink and Swanwater Lake

was established in the first trace, the data from the second trace confirms that the River Rise is a point of resurgence for some portion of the Santa Fe River flow diverted into O'Leary Sink. If, we also detected at two locations 30 m and 330 m downstream of the River Rise, revealing two possible resurgence points of diverted Santa Fe River water.

The tracer response plots for the locations sampled, (shown in Figure 10), are not "ideal" smooth response curves such as those associated with the sinkholes monitored in the first tracer study. Instead, they are characterized by multiple peaks indicating the episodic arrival of the tracer at all three locations. These data suggest that the underground flow of the Santa Fe River between Sweetwater Lake and the River Rise does not take a singular path, but possibly multiple pathways.

Jim's Sink to Santa Fe River Soils

As a result of the first two water tracing experiments, a connection between all the sinks monitored in the park was established. However, beyond Jim's Sink it appeared that there was some ground water segmentation or underground Santa Fe River water diverted in this complex system. To better establish the relationships between ground water and underground Santa Fe River water downstream of Jim's Sink, another water tracing experiment was undertaken. In addition, this tracing experiment provided the opportunity

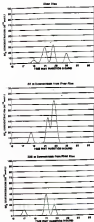


Figure 19. concentration response curves for Jim's fish exposed.

to compare rhodamine WT dye, the most frequently used ground water tracer, and SF_6 , the newly developing ground water tracing technique.

The tracer solution was prepared as described previously and a 10% solution of pure rhodamine WT was added to this barrel. The SF_6 and rhodamine WT solution was introduced to the sink via tubes taking at approximately 1.75-2 L/min. The add-depth injection of this SF_6 /rhodamine solution into the sink was continuous over the next two hours. Two hours prior to tracer injection, packets filled with activated charcoal were placed at various spilling points in Two Mile Sink, Sandstone Lake, the River Sink and boils in the Santa Fe River 100 m downstream of the River Sink, in order to establish background readings for rhodamine WT. After completing the injection, these packets were collected and replaced. These packets were rinsed with water and stored on ice until their analysis.

Based upon the results of the two earlier water tracing experiments, a sampling scheme was established at each of the four locations. SF_6 water samples were collected about every half-hour beginning about 10 hours after injection at Two-mile and ending about 10 hours after injection at the boils in the lower Santa Fe River. The rhodamine WT packets were changed at about four hour intervals over that same sampling period.

SF_6 was detected at two mile mark, Sweetwater Lake, the Santa Fe River Rise, and at the mile 250 station below the River Rise. The concentration response curves for these locations are shown in Figures 10 and 11. Arrived times for the leading edge of the tracer (TL), the travel time of the centroid of the SF_6 mass (T), and the total tracer passage time are shown in Table 7. The average SF_6 travel velocities calculated from the travel times of the centroid of the SF_6 mass and the straight line distance between the sinks are also shown in Table 7. Rhodamine WT dye was also detected at all the sampling sites. These results also are shown in Figures 10 and 11. Values were recorded as "no response", "weak", "moderate", "strong" and "very strong" as only relative values of intensity could be obtained due to the limitations of the analytical equipment. The rhodamine sample packets were collected at four hour intervals which imposes a delayed peak response curve over that of the SF_6 sample curves. This delay in rhodamine is a response to the sampling interval not the travel rate of the tracer.

The arrival of the tracer front and the most discerning peak occurred 10 and 45 minutes later 450m downstream than at the Santa Fe River Rise. SF_6 detected at the mile 250 possibly represents the mass loss of tracer detected at the river's resurgence. The quantity of tracer recovered at the mile is 80% of the volume of the tracer recovered at the rise, which is a consequence of gas exchange between the

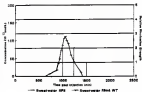
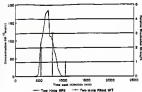


Figure 18. Concentration response curves for Dia's 2000 experiment.

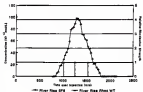
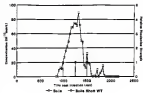


Figure K1. Concentration response curves for Site's Sink against Lead.

Table 7. BF_3 travel times for Jim's Sink to Santa Fe River Sink Experiment.

Site	Distance below Jim's Sink		T_1 (min)	T_2 (min)	Passage (min)	T (min)	App. vel. (m/d)
	(m)						
Tom Hole	1175		425	495	405	425	0.91
Swamp	2400		710	1050	840	1000	0.94
River B.	4100		870	1440	1080	1310	0.90
ECIS	4500		910	1590	1080	1410	0.88

T_1 = time to leading edge of tracer.

T_2 = travel time at midpoint of the BF_3 zone.

T , travel times were calculated from the midpoint of the two hour BF_3 injection (48 min).

Estimated mean underground flow velocity between Jim's Sink and the Santa Fe River Sink is 0.9 km/day.

river and the atmosphere between the two sampling locations. A rough estimate of gas transfer was determined of SF_6 over the 150 m distance, according to equation 8:

$$(9)$$

$$\ln(v/a \ln\{[SF_6]_{up} Q_{up}/[SF_6]_{down} (Q_{down})\})$$

where

k is the gas transfer velocity;

h is the mean depth (3.1 m);

v is the stream velocity (0.124 m/s);

x is the interval under investigation (150 m);

Q_{up} is the discharge at the River Rise (3.3 m³/s);

Q_{down} is the discharge at the baile (3.3 m³/s);

$[SF_6]_{up}$ is the peak concentration of SF_6 at the River Rise (700×10^{-10} mol/L); and

$[SF_6]_{down}$ is the peak concentration of SF_6 at the baile (170×10^{-10} mol/L).

The calculation yielded a gas transfer coefficient of 17.6 m/d, which is lower than the value of 27.5 m/d obtained in an earlier gas exchange experiment carried out along a 5 km section of the Santa Fe River below the River Rise. At that time stream discharge exceeded 10 m³/s (Ellis et al., 1993).

Examination of the SF_6 concentration response curve at the baile (Figure 12) reveals two additional peaks on the trailing limb of the response curve, suggesting that some of the subsurface flow of the Santa Fe River is discharged to the main stem of the river at this point. This finding is supported by discharge measurements obtained during the experiment, which reflect an increase of 0.5 m³/s from 3.8 m³/s at the Santa Fe River Rise to 4.3 m³/s at the baile.

Examination of the ^{86}Sr response curves for each sampling location reveal some interesting points (Figure 10 and 11). The Hole Sink and Sweetwater Lake curves are characterized by a single sharp peak. The curve for the Santa Fe River Rise, however is characterized by a sharp rise to a peak and then a more gradual concentration increase to a second peak. This second shape suggests that two partially overlapping response curves are depicted at the Santa Fe River Rise. At the Hole Sink a downstream peak separation is more pronounced and the peaks are distinguishable in the concentration response curve. Most of the underground river flow resurfaces at the River Rise, but a small flow may be diverted via minor pathways to a discharge point 100 m below the rise.

Additional support for a two conduit flow route is provided by comparing the total mass ^{86}Sr recovered at each of the sampling sites. If there is equivalent discharge at the Hole Sink, Sweetwater Lake, and the River Rise, the quantity of ^{86}Sr recovered is 14.7 ± 10^{-4} mol (129 ± 10^{-3} g), 13.0 ± 10^{-4} mol (108 ± 10^{-3} g), and 16.3 ± 10^{-4} mol (138 ± 10^{-3} g), respectively. Since the mass of the tracer at the Santa Fe River Rise is greater than at either sink alone, the underground flow of the river must follow more than one flow path. Discharge at the three sampling locations would not be consistent but less at the Hole Sink and Sweetwater Lake than at the River Rise, if this is the case. However,

The estimates of the quantity of tracer recovered at Two Mile Sink and Sweetwater Lake would be too high in such a scenario. The mass of tracer recovered at the Santa Fe River Rim, however, would still be greater than at either Two Mile Sink or Sweetwater Lake. Thus the conclusion that the subterranean flow of the Santa Fe River follows more than one route between Jim's Sink and the River Rim is still valid.

Summary of Water Tracing

The artificial tracer SF_6 was used successfully in three water tracing investigations in the Santa Fe River Basin to track the subterranean pathway of the Santa Fe River between O'Leary Sink and the River Rim of the Santa Fe River. The results of the water tracing experiments carried out indicate that the subterranean flow path of the Santa Fe River follows a single corridor flow conduit from its existing point at O'Leary Sink to Jim's Sink. After Jim's Sink, the underground flow path splits following one conduit at Two Mile Sink and then to the Santa Fe River Rim, and a second pathway to Sweetwater Lake and then the River Rim. The sub-surface flow pattern that is tentatively proposed is shown in Figure 12. These data confirm that (1) the Santa Fe River Rim is the primary resurgence of the underground flow of the Santa Fe River and (2) suggest that a small portion of the underground river enters the main stem of the

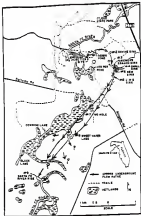


Figure 10. Flow pattern of the underground Santa Fe River through O'Neal State Park.

Santa Fe River about 200 m below the River Rise at a spot marked by holes in the River.

Average flow velocities calculated ranged from 1.8 to 1.4 m/day. Such rapid ground water movement renders the water resources of the Santa Fe River basin vulnerable to contamination and underscores the urgent need for careful management practices.

The results of this research further confirm that SF_6 , which is safe, chemically and biologically inert, and capable of being detected in extremely low concentrations, is well suited for water tracing applications in karst terrain. In comparison to fluorescent dye tracers, such as rhodamine WT, SF_6 has the advantages of detectability at low concentrations and none of the interference problems associated with organic acids, dissolved particulates, and aquifer material that can occur with fluorescent dyes. This is particularly helpful in hydrologic settings such as the Santa Fe River with high organic acid concentrations.

SF_6 is a volatile compound as gas exchange occurs when ground water is exposed to the atmosphere in karst windows. In hydrologic settings where there is no contact between ground water and the atmosphere, however, SF_6 may have potential as a quantitative tracer. SF_6 may also have value in determining whether a hydrologic flow network is completely developed in the volcanic zone or is a partially flooded setting, as is sometimes the case in dikes or steep

gradient systems. Further research is needed to properly evaluate the performance of NF_3 in comparison to other proven tracers and to develop additional hydrologic applications for this compound.

Flow Component Analysis

After the completion of the tracing experiments within O'Leary State Park it appeared that the subsurface flow path of the Santa Fe River had been characterized. However, its relationship with the ground water along its course had remained unresolved. In order to further establish the link between the two sources of water in the park several flow component analysis experiments were completed. The experiments used both relatively simple techniques such as water temperature readings and more complicated techniques such as $^3\text{H}_2$, $^{18}\text{O}_2$, and major cation concentration analysis. These techniques were employed because of their relative ease of use and their potential to separate or indicate different water types.

Water-Sample Collection

Water samples were taken from 18 different water filled features throughout the park and from the parks main office coveet which taps the Floridan Aquifer in the region (Figure 15; Edie Hendrick, personal communication, 1981). Samples were drawn into graduated cylinders as previously described

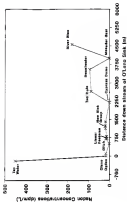


Figure 16. Radon-222 concentrations for early features found throughout the park.

and analyzed as before (see Materials and Methods Chapter I and Figure 17).

The results of this transect show the ^{222}Rn levels at each location (Figure 14). The top water sample in this transect reflects that of typical ground water conditions in the area (Eller, personal communication, 1983). The ^{222}Rn concentrations found throughout the park in its upstream section (eg. O'Leary Sink, Farlow Sink/linear features, New Sink group including Jim's Sink) are essentially near to atmospheric background levels. However, beyond Jim's Sink (eg. Two Hole, Sweetwater Lake and River Sink) the ^{222}Rn levels steadily increase towards the ground water lens.

This increase in radon levels suggests an influx of ground water into these sinks along the subterranean path of the Santa Fe River. The surface features, (cypress dome and meander scar, having low ^{222}Rn levels, downstream of Jim's Sink) also confirm that the surface water is not directly, hydrologically connected to the ground water in this region of the park.

^{222}Rn Transect

Top water samples were collected from 17 different water filled features located throughout O'Leary State Park (Figure 15). Each sample was collected at a depth of about 1.0 m where possible. Samples were collected and analyzed

as previously described. In theory, the oxygen isotope values for the ground water and the surface water should be different because of the evaporative and precipitation effects on the composition of the surface water. The ground water values will have a characteristic signature value based primarily upon the source of the ground water and any mixing the water has had with other ground water. The surface water on the other hand will have a signature value based primarily upon the $\delta^{18}\text{O}$ values of the precipitation, and any subsequent or previous rain events and the evaporative effects on the surface water body. The surface water, if it has undergone substantial evaporation will relinquish the lighter isotope $\delta^{18}\text{O}$ to the atmosphere making the residual water heavier or more enriched in $\delta^{18}\text{O}$ (Fisher, 1948). The process causes the $\delta^{18}\text{O}$ values to increase relative to standard mean ocean water values (SMOW). Because this water has remained at the surface and has not been mixed with either pure ground water or with new precipitation it can easily be distinguished from ground water.

Figure 18 shows the $\delta^{18}\text{O}$ values for the water features sampled in Ocala State Park. In this figure there are three distinct groups of water. The first group appears to be pure ground water and is represented by the top water, which is drawn from the Floridan Aquifer. The second group is surface water and is represented by the opposite dam, meander pool and to some degree the drainage ditch. The

third group is a mixture of the surface water and the ground water and is represented by essentially all other features labelled on the figure.

These results suggest that there are three different types of water within O'Leary State Park and that there is a contribution of ground water to the underground Santa Fe River water beyond Sweetwater Lake.

Cation Concentrations

Total cation concentrations as well as cation ratios were evaluated. Al^{+++} , Ca^{++} , Mg^{++} , K^+ , and Na^+ were detected at all 21 locations (Figure 10). Of these, Ca^{++} appeared to be the element that best separated ground water and surface water components. All other elements appeared to give inconsistent results. Several element ratios were also evaluated in order to separate water types (Table 8). According to Fetter (1968) ratios of Mg/Ca , Na/K and $(Ca+Mg)/(K+Na)$ have been used to establish water properties. Mg/Ca ratios of 0.3-0.7 indicate a limestone source, 0.7-0.9 ratios indicate dolomite and ratios >0.9 indicate a silicate source rock (Fetter, 1968; Fetz, 1968). Na/K ratios equaling 49 indicate seawater, ratios equal to 18 indicate rainwater and those between 18 and 25 indicate water that is close to its recharge area. In addition, $(Ca+Mg)/(K+Na)$ values greater than 1.0 also indicate that water is close to its recharge area. The Na/K ratio and $(Ca+Mg)/(K+Na)$ ratio

Table 3. Sulfon ratios for locations throughout O'Leary State Park.

Location	mg/L Mg/Ca	mg/L Sr/S	mg/L (Ca+Mg)/(Sr+Sr)
Tap water	0.000	0.000	100.000
O'Leary Sink	1.080	10.230	9.217
Swineage ditch	1.410	13.430	4.089
Open Pond	1.170	17.900	6.004
Barina Sink	0.460	14.760	12.220
Linear Feature #1	0.700	26.400	35.260
Linear Feature #2	0.400	24.900	12.070
Linear Feature #3	0.700	16.510	10.700
Panorama Branch	0.000	24.840	11.410
Small Sink	1.040	14.540	12.100
Box Sink	1.000	17.900	11.000
Jim's Sink	0.940	14.700	12.200
Cypress Swamp #1	0.340	0.770	29.500
Two Hole Sink	0.470	28.830	70.120
Wanderer Sink #1	1.070	40.070	3.000
Black Lake	0.170	24.800	104.000
Cypress Swamp #2	0.000	28.400	23.220
Swartwater Lake	0.000	24.710	24.070
River Sink	0.400	26.770	10.000
River Sink = 100m	0.710	19.900	27.440
River Sink = 100m	0.600	18.420	20.420
Presipitation	0.000	0.000	0.000
Average	0.800	19.550	34.070
std. dev.	0.460	17.400	41.000

Mg/Ca = 0.0 - 0.7, limestone

Mg/Ca = 0.7 - 0.9, dolomite

Mg/Ca = > 0.9, silicate

Sr/S = 47, evaporite

Sr/S = 30, dolomite

Sr/S = 15-25, cGess to calc water

(Ca+Mg)/(Sr+Sr) = > 1.0, near recharge

(values from Fetter, 1988)

yielded varying results with no apparent trends or correlations.

Using the Mg/Ca ratio, ground water and surface water groupings of water bodies can be delineated. Those features having a ratio of greater than one reflect the water chemistry of surface water fed bodies. These include: O'Leary Sink, drainage ditch, Cypress Pond, Small Sink, and the meander scar. Those features having a Mg/Ca ratio of less than one reflect a ground water influenced feature. These features include: tap water, linear features 1, 2, and 3, Two Hole Sink and the River Sink sampling locations.

Ternary diagrams also reveal distinct types of water groups (Fetters, 1988; Fogg, 1992). When plotted, the cation concentrations of Mg^{2+} , Ca^{2+} and $Na^{+}+K^{+}$ show three distinct types of water, calcium dominated type, a sodium or potassium type and a non-dominant ion type which constitutes the largest number of samples in O'Leary (Figure 54). Those features that are dominated by the calcium ions are the dominance features: Two Hole Sink, Black Lake, Cypress Pond #1 and the upstream tap water site that was taken from the ranger house at the park's northern entrance. The non-dominant ion features included the three linear features, the three River Sink samples, and the upstream small (mainline Sink, Sweetwater Lake, Jim's Sink, New Sink, Foreman Branch Sink). The sodium and potassium dominant features primarily

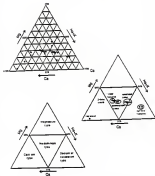


Figure 16. Calcium concentrations at all locations throughout O'Leary State Park (top), groupings of selected features through the park (bottom) and dominant ice areas within binary diagram (bottom, after Fetter, 1988 and Kola, 1992).

include the surficial features, such as the meander scars and the drainage ditches.

The middle diagram in Figure 24 reveals a trend of increasing Ca^{++} (ground water) influence with increasing distance through the park. The surficial features represent the surface and meadow water type and the top water sample represents the ground water and meadow. The upstream slacks, those above Jim's Sink, more closely resemble the chemical signatures of the surface water in the area. The downstream slacks, namely Sweetwater Lake and the three River Mile locations more closely resemble the chemical signature of the ground water (top water sample). The linear features which lie within 100m of Ravine Sink more closely resemble the nature of the ground water as well.

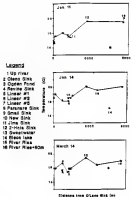
Temperature Tracer

In a previous study, Shiroin (1982) reported that it was possible to detect ground water in all the slacks monitored in this study during a period when Santa Fe River discharge in Gila State Park was temporarily, but completely dammed due to construction in the upper reaches of the Santa Fe River. To determine the extent that the underground Santa Fe River flow is regulated by ground water, temperature measurements were utilized to calculate the relative proportions of ground water found in those slacks hydrologically connected to the underground pathway of

the Santa Fe River. Five additional water-filled marsh features in O'Leary State Park were also monitored for comparison purposes.

The first set of 13 water temperature measurements was taken on January 11, 1982. The air temperature was 11°C and the water in O'Leary Sink was 10°C. Ground water was assumed to be 10°C (Fernald and Pettus, 1984; Florida Geological Survey, 1981). The temperature measurements revealed that these sinks are hydrologic contact with the underground flow of the Santa Fe River between Opan Pond and Jim's Sink were warmer than the Santa Fe River by about 2.5°C, suggesting some ground water mixing with the underground flow of the Santa Fe River (Figure 17). The next temperature increases in water temperature, however, occurred at Two Hole Sink. The water temperature in Two Hole Sink was 1.5°C greater than the previous sink measured, Jim's Sink. Black Lake was measured because it had a minimum depth of only three meters making it a surficial feature not in hydrologic contact with the underground flow of the Santa Fe River. Black Lake recorded a temperature much lower than ground water, 14°C.

Two additional temperature readings were taken on January 14 and March 14, 1982. The ambient air temperature was warmer, however, so the temperature gradients were dissipated and the results, although similar, are less dramatic. On January 14, a significant averaging of temperatures may have taken place due to a previous night's



rainfall in the area of 1.1 m (personal communication, Dale Kendrick, 1988).

Because the Santa Fe River follows a subterranean flow path for at least five kilometers before resurfacing at the River Mile, some factors in addition to mixing with warmer ground water may result in elevated temperatures. These include the type of flow, the surface area of the underground water in contact with the walls of its conduit and exposure of ground water to the atmosphere. The least important of these is the transfer of heat from the limestone aquifer to the underground stream across the rock/water boundary. This is because limestone has a very low heat conductivity (8,000 gram calories per centimeter degree second, Finner and Sargent, 1984; Lohreyer, 1984; Lohreyer and Schuchman, 1981). In fact, pure often the surrounding rocks act as insulation to the ground water system (Lohreyer, 1988).

Assuming that the warming could not have been achieved by contact with the limestone aquifer, and a relatively short time period which ground water is exposed to the atmosphere (about 48 hours), it is suggested that mixing of surface water with warmer ground water offers the best explanation for the increased temperatures observed. Calculations of ratios in percent between ground water and Santa Fe River water measured at each mile can be accomplished by assuming that the measured temperatures of

O'Leary Sink (18°C) and River Sink (12°C) are respectively the minimum and maximum temperatures attainable by the water in this region. Therefore, a one degree increase in the measured sink water temperature would be equal to about a 15% contribution of ground water. For example, at Ravine Sink, the temperature increase of 2°C to 18°C represents a 15% ground water influx to the underground flow of the Santa Fe River. Based on the temperature measurements, this ratio of about 49/48 or 45/35 (ground water/underground Santa Fe River water) remains fairly uniform through Jim's Sink, a distance of 1.2 km. At Two Hole Sink, however, the water temperature rises 4°C from 14°C at O'Leary Sink to 18°C, suggesting 80% ground water augmentation. The water temperature at the River Sink is 12°C, which is the same as local ground water temperatures. This finding suggests that there is no original Santa Fe River water left at this point and that it has disappeared or continued elsewhere in its underground path. However, this can not be true because the SF_6 tracing experiments revealed measurable amounts of SF_6 at the River Sink, and demonstrated a hydraulic connection between O'Leary Sink and the River Sink. Temperature measurements confirm that Black Lake, which remains colder than the other downstream sinks, is only a surface feature with no ground water or Santa Fe River water component. This finding is corroborated by the fact that its maximum depth is only three meters (McIlwain, 1949).

Computer Modeling

Computer modeling of an aquifer requires making several assumptions about aquifer parameters. These assumptions include: isotropic conductivity, constant head or constant flux boundaries, relatively homogeneous aquifer material, and variable ranges of hydraulic conductivity values (cm/s or ft/d).

Numerous scenarios were attempted to model the area based on the water flow velocities calculated from the tracing experiments. Because of the anisotropic conditions that exist and the complex interactions between ground and surface water the area, it was impossible to model with the current software packages available.

The initial model setup shows the distribution of the discretized area, boundary conditions, water table elevations and surface water features (Figure 18). This model set up was completed using MODFLOW[®] (Harbaugh and Miller, 1980) a computer aided design software package for ground water modeling. Because there is no confining layer in the modeled area a two dimensional model setup was produced. A three dimensional model is normally setup when two or more aquifers are found within a specific area. This pre-processed input file was then sent to the main computer program MOD[®] (Method of Characteristics, Rodhe and Rodhe, 1981) for interpretation.

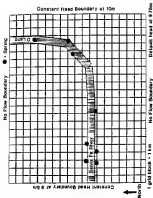


Figure 18. Computer model map up (far the western) side of the river region between 8°15'N and 8°16'N.

In theory the constant head boundaries at the western and eastern edge of the mapped area act as the driving forces of water flow. A default head elevation is assigned to all other gridded areas and the computer then calculates the predicted head values over a certain time interval based upon the aquifer's physical properties (thickness, hydraulic conductivity, storativity, leakage, recharge). In most non-karstic aquifer settings this process is relatively straight-forward.

In this karstic region hydraulic conductivities of the aquifer may vary by several orders of magnitude within the same aquifer (Burr and Klock, 1991). Moreover, these trends in conductivities have no obvious geologic or topographic boundaries. To further complicate this karstic setting, numerous springs are located in the area which creates another modeling challenge. This challenge is created because the computer model does not have a "spring" parameter which allows for the accurate depiction of a spring in the model. Instead, the springs were modeled as recharging wells to the river with their recharge values equivalent to each springs output. The river, however, as previously noted, is directly connected to the underlying aquifer and in reality may fluctuate with the top of the potentiometric surface of the Floridan Aquifer.

Because of the complexity of the model and the abnormally high hydraulic conductivities the computer

program was unable to process the data. The program failed for several reasons. The reasons include first, the computer program has a built-in mass balance system that allows for only a 1% error in the amount of water going into and coming from the aquifer. The abnormally high conductivities of the aquifer and the numerous springs along the stream caused a gross imbalance in the water exiting the aquifer. Second, the recharging wells to the surface effectively elevated the ground water levels to unrealistic levels. These unrealistic levels created "mounds" of water surrounding each spring. Third, because surface water and ground water are one in the same in many cases, they can not be quantitatively described and accounted for in the model. This third problem again results in an imbalance system in the model. Fourth, the anisotropic conditions of the aquifer were not reproducible in computer modeling format because of the general lack of knowledge of the three dimensional location of conduit patterns surrounding the Santa Fe River. This fourth problem lead to an unrealistic homogeneous aquifer setting.

Numerous attempts were made to adjust the model to produce some output, however all were unsuccessful. It is now understood that even with all the data collected from this report and many others, the area in many ways is still perplexing. These results are corroborated by several authors that have suggested that no current ground water

computer model can accurately characterize baritic conditions (James Quinlan, personal communication, 1994; Paul Lupton, personal communication, 1994).

Isotopic Studies

Sampling locations along the Santa Fe River for the first experiment are shown in Figure 19. Figure 20 shows the Sr_2 , ^{86}Sr and stream-flow profiles for this reach. Bernabé Springs is the only documented major contributor of ground water to the Santa Fe River along this reach. However, distinct peaks in the ^{86}Sr profile reveal locations of unrecorded ground water inflow. The stream flow data indicates that the Santa Fe River flow is increased by as much as $15 \text{ m}^3/\text{s}$ upstream of Bernabé Springs. Sr_2 concentrations decline downstream of the injection point due to gas exchange, where increases in the Sr_2 concentrations are noted except at 1.75 km and 4.5 km (Columbia Springs). The increase in Sr_2 concentrations may reflect incomplete lateral mixing in the stream or the return flow previously diverted from the main stream channel to conduits in the limestone aquifer further upstream. At 1.75 km and 4.15 km, two large syphons where stream flow is directed underground are clearly visible. Stream water lost to sub-channel conduit flow results in no change in tracer concentrations in the stream at the point of flow loss. Downstream of the flow loss point, Sr_2 concentrations continue to decline in

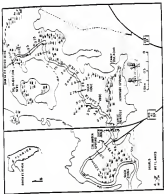


Figure 25. Sampling locations for the fifth generation experiment (after Nelson et al., 1962).

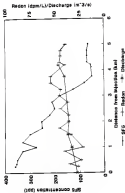


Figure 48. Redox Potential and redox potential for the client monitoring system.

the stream-flow due to gas exchange.

SF_6 laden stream flow diverted underground, however, is removed from the atmosphere's contact and gas exchange no longer occurs. SF_6 concentrations therefore remain the same in the underground flow, except where dilution due to mixing with ground water takes place. The inflex of return flow of previous surface water to the Santa Fe River is indicated by SF_6 concentrations that are higher than concentrations in samples collected in the river upstream, which will have a declined due to gas exchange. Columbia Spring discharges to the Santa Fe River and represents the return of stream flow down underground by means of a siphon in the Santa Fe River at 4.15 km is shown by elevated SF_6 concentrations at 4.5 km.

Sampling locations for the second reservation experiment are shown in figure 41 and the SF_6 , ^{222}Rn and stream flow profiles are shown in figure 42. Both types of SF_6 profiles are shown in order to represent the integrated and grab sampling results. A number of springs add to stream flow along this reach of the Santa Fe River. The ^{222}Rn peaks in figure 42 mark the locations of known springs. Unlike the first reservation experiment, SF_6 concentrations do not decline as expected (figure 43). The SF_6 profiles are instead characterized by many spikes possibly caused by poor mixing of ground water with stream flow. Some locations of the SF_6 peaks, however, closely correspond with the ^{222}Rn

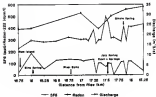


Figure 13. Sulfate, radon, and exchange profiles for the first cessation experiment.

peaks and known springs. For example, the SF_6 peak at 17.15km matches the ^{222}Rn peak that represents ground water delivery from the Devil's Ear, Devil's Eye and Little Devil springs. Another SF_6 peak centered around 17.28 km corresponds to Glade Spring.

The occurrence of ^{222}Rn and SF_6 concentrations together suggests that discharge from the Devil's Ear, Devil's Eye, Little Devil and Glade Springs is not pure ground water, but a mixture of ground water and Santa Fe River water, which was diverted underground at locations upstream. Work completed by Kincaid (1984) supports this theory. Although there is no direct evidence of seeps in the Santa Fe River along this reach, the stream flow profile indicated (see between 17.00 km and 17.35 km (Figure 42). An extensive cave system, the Devil's Ear Cave System, extends beneath the Santa Fe River along the second reservation segment. Several springs, including July, Little Devil and Devil's Ear are physically connected by a network of conduits to the cave system (Kincaid, 1984). Cave divers have reported intrusions of Lewis and Clark water from the Santa Fe River to the Devil's Ear Cave. The observations coupled with the ^{222}Rn and SF_6 data provides evidence of the influence of the Devil's Ear Cave system of interactions between ground water and stream flow in this part of the Santa Fe River (Kincaid, 1984). A more detailed description of the reservation coefficients calculated and the relationship

between the Santa Fe River with ground water along this reach of river is discussed in Kincaid (1994).

Gas Transfer

The gas transfer velocity (k) for SF_6 during plateau concentrations for each continuous injection was determined according to equation 4. Ground water inflow along the study reaches increased stream-flow and diluted the transfer. In addition, there is discharge from riparian wetlands to the Santa Fe River. Naturally occurring ^{222}Rn was used to locate or ground water delivery along each reach. Adjusted stream-flow values, based on the stream gaging effort, accounted for the dilution by ground water in calculating the gas transfer velocities using SF_6 . Table 3 provides the stream gaging data for the Santa Fe River.

The gas transfer velocity of 81.5 m/d was calculated for the River flow restoration experiment between 0.49 km and 1.15 km. This length of reach was used to avoid possible mixing problems at the beginning of the reach and the influence of returning SF_6 -labelled stream flow at Columbia Springs.

The Devil's Bar gate system exerts a controlling influence over interactions between ground water and stream flow along the Santa Fe River based on the ^{222}Rn and SF_6 data. Also, in this region of study the spring discharge should be regarded as a dynamic source of ground water and

Table 3. Access gaging data for the Santa Fe River,
First Reservoir Experiment, River Mile

Distance from River Mile (km)	Discharge(m^3/s)	Depth(m)	Velocity(m/s)
0.08	27.6	1.78	0.148
1.0	32.4	1.90	0.169
1.8	35.6	1.80	0.178
2.0	40.8	2.00	0.204
3.78	43.2	2.40	0.180
4.13	47.6	1.96	0.242

Second Reservoir Experiment, Run Related to Kinetic Energy

Distance from River Mile (km)	Discharge(m^3/s)	Depth(m)	Velocity(m/s)
15.75	22.8	1.66	0.138
16.00	22.2	1.50	0.148
17.00	20.7	1.66	0.124
17.10	20.4	0.74	0.276
17.60	20.2	1.80	0.111
17.90	20.5	0.44	0.468
18.00	22.0	2.02	0.109

Santa Fe River water rather than pure ground water (Klaczko, 1984). Because this reach involves complicated interactions of surface and ground water it was not possible to determine the extent to which stream flow entered conduits of the Devil's Bar Cave nor to accurately address the quantity of pure ground water discharge along the reach. In an accompanying study by Klaczko (1984) a more detailed investigation of the respiration and gas exchange values for this reach of river was completed. His work revealed an average k value of 4.48 m^3/d and an average R_g value of 3.79 day^{-1} for this reach of river.

Corrected discharge values (shown in Table 5) were used in the gas exchange calculations in an attempt to take into account stream flow loss and the degree to which tracer concentrations are decreased by dilution resulting from ground water seepage. This method produced gas transfer velocities of -13.1 m^3/d and 1.4 m^3/d for the integrated and grab sampling R_g data, respectively. These negative values suggest that gas exchange is negligible along this short reach and that the decline in concentrations observed is due entirely to dilution by ground water. Based on the measured stream flow values for the reach gas exchange calculations do not adequately account for dilution by ground water and thus over estimate the value of k . On the other hand, the adjusted stream flow values do not account for the mixing of Santa Fe River water

with pure ground water in the Devil's Den cave and the subsequent discharge of some mixture of the two water types along the reach.

Table 10 and 11 show the calculated values of k in m^3/d for intervals between the stream gaging stations in the Santa Fe River. As previously mentioned comparisons of k values between stream segments underscores the degree of variability induced by the non-uniformity of the stream channel and incomplete mixing of ground water with stream flow.

Although ^{222}Rn was used to estimate gas exchange in the river, an attempt was made in the San Isabel reach of the Santa Fe River because of the dense proximity and great number of ground water inflows to the Santa Fe River. These factors made it impossible to determine the rate of gas exchange between pulses of ^{222}Rn in the stream. The interested reader is referred to Rincold (1984) for a more detailed discussion of factors involved in estimating gas exchange in this portion of the Santa Fe River.

Resurrection Coufficients

Santa Fe River gas transfer velocities determined using O_2 were related to the rate of oxygen uptake and expressed as respiration coefficients (R_g). Temperature strongly controls the gas transfer coefficient determined for these gaseous streams used in the stream respiration studies. The

Table 10. Values of k in meters per day for intervals between the stream gauging locations in the first recession experiment.

Point	Distance from Injection (m)	Interval (m)	Discharge (m^3/s)	SP ($gmol/l$)	Transfer Velocity k (m/d)
1	0.00		27.45	345	
8	1.00	0.70	20.40	277	20.3
14	2.05	1.05	14.45	255	1.5
27	3.7	1.65	48.12	49	22.7

Table 13. Values of K in meters per day for intervals between the stream-gaging locations in the first restoration experiment.

Sta.	Distance from Injunct. (km)	Int. (km)	Disch. (m^3/s)	SF, (mm 2 /s)		Transfer Velocity (m/d)	
				meas. [42] ^a	Int. [400]	Int. [400]	
8	0.18		25.1	1164/1164			
6	1.26	1.08	20.7	421	782	0.5	2.2
13	1.66	0.38	22.8/22.7	495	742	1.7	2.8
17	1.88	0.38	26.2/27.2	472	882	-20.8/28.8	
21	2.18	0.38	22.8/42.4	"	421		
24	2.8	0.38	22.8/41.4	325	482		

^aThe measured stream flow data reflect the loss of flow along the second restoration experiment at point 17.18 km, which corresponds to 1.4 km below the SF₁ injection. The adjusted stream flow values take transfer velocity by the locus of ground water into consideration in estimating gas transfer velocities. Using the interpreted and grab sampling SF₁ data with measured stream flow data, the gas exchange transfer velocities calculated for the second experiment between San Isidro and Gloria Springs area are 7.8 m/d and 19.0 m/d, respectively. When the adjusted discharge values are used in the calculation, however, negative gas transfer velocities of -17.1 m/d and -1.0 m/d are estimated for the interpreted and grab sampling SF₁ data, respectively.

^b not available due to questionable data.

higher the temperature, the faster the gas exchange process. In order to compare gas exchange coefficients for different gases or to use one gas exchange coefficient to predict another a dimensionless ratio, the Schmidt number (Sc), was used (Schweil, 1964; Wassinkhof, 1968; Flood, 1964). The schmidt number is defined as the kinematic viscosity of water (ν) divided by the molecular diffusivity of the gas (D). Since both ν and D are temperature dependent, the Schmidt number corrects for the temperature and species dependence of the gas under consideration (Jahn et al., 1977; Wassinkhof, 1968). The Schmidt numbers for HF_4 , ^{222}Rn and O_2 for temperatures ranging between 15 and 17 degrees Celsius are found in Table 13.

There are many models available to describe the relationship between the gas transfer velocity (k) and the Schmidt number (Sc) (Riley et al., 1968). In this work, the correction of the exchange coefficient is based upon equation 9.

$$(9)$$

$$k_1/k_2 =$$

where

k = transfer velocity,

Sc = Schmidt number,

$n = -0.5$ and depends on the turbulence at the air/water interface.

Table 13. Comparison of denitrification estimates for N_2 , ^{222}Rn , and C_2 at selected temperatures.

Temperature $^{\circ}\text{C}$	N_2	^{222}Rn	C_2
18	1288	1680	849
20	838	838	531
25	742	676	428
27	442	427	276

The denitrification coefficient was calculated using the following equation (from Kilham et al., 1983).

(10)

$$E_d = k (D\text{F}_d) / k (D\text{C}_2/\text{Sch}_d)^{0.44}$$

where

E_d = denitrification coefficient, day^{-1} ;

k = gas transfer velocity, m^2/d ;

h = average stream depth, m ;

Sc = Schmidt number for the indicated gas at 20°C (water temperature of the river).

The Santa Fe River's gas transfer velocity and corresponding denitrification coefficient is $27.8 \text{ m}^2/\text{d}$ and 28.7 day^{-1} , with $w = 0.12 \text{ m/s}$, $h = 2.1 \text{ m}$, $q = 48.0 \text{ m}^3/\text{s}$, and $t = 21^{\circ}\text{C}$ in the eastern reaches of the river. Table 13 provides a comparison of denitrification coefficients from Florida and other streams using volatile tracers. Using a variety of tracers the denitrification coefficients based on N_2 measurements are within the same order of magnitude as E_d

values given for other streams with the exception of the West Fork of the Walker Branch, Oak Ridge TN. The typical K_d values range from 118 to 138 day⁻¹, using SF₆, propane and ethane as gaseous tracers (Wassinkhof et al., 1988; Garman et al., 1992). Therefore the K_d values for this stream are about an order of magnitude greater than other published values for different streams.

Many predictive equations have been developed for specific streams that permit estimation of gas transfer and respiration coefficients. These equations typically relate respiration coefficients to several easily measurable physical and hydraulic parameters of a stream. Table 14 shows respiration coefficients (K_d) values determined for the two river reaches based on different predictive models available in the literature. The calculated K_d values vary considerably. None of the equations referenced in Table 14 were suitable indicators of the respiration coefficients determined for the first Santa Fe River experiment, through experimentation. The basic statistics for the predicted K_d values for this reach were a mean of 1.88 day⁻¹, a standard deviation of 2.88 day⁻¹, and a median of 1.15 day⁻¹. If these statistics are compared to the values estimated from the SF₆ tracer experiment (16.7 day⁻¹), it can be concluded that all these models underestimate K_d for this reach of the Santa Fe River.

Table 13. Comparison of selected stress relaxation coefficients determined through the use of volatile tracers [from Miller et al., 1983].

Stream	ν (%/s)	δ (s)	σ (μ^2 /s)	λ_0 (s^{-1})	λ (%/s)	tracer	T °C	Ref.
Wetzel	1.38	2.4	2.72	14.2	1.32	CH_3Cl	22	1
Wetzel	2.48	4.1	28.9	9.3	1.22	CH_3Cl	22	1
Barnes	3.08	9.3	8.62	7.4	1.22	propane	25	3
R. Mason	2.24	2.98	2.82	12.2	2.42	ethylene	27	3
Jackson River St.	1.12	9.42		3.3	2.12	H_2O	25	4
W. Fork/ Walker Cr.	0.82	2.22	0.22	124	12.2	SF_6	22	4
W. Fork/ Walker Cr.	0.2			122		propane		7
W. Fork/ Walker Cr.	0.2			122		ethane		7
Aspen River	0.22	2.22	0.22	2.4	1.2	Freon-12	5	6
Alligator Creek, FL		2.22	2.22	2.2		propane		8
John River Cr. FL		2.42	2.22	2.4		propane		8
Cowboy Ck., Creek, FL		2.22	2.22	12.2		propane		8
Panola R. FL		2.22	2.22	2.2		propane		8

References

1. Miller, 1984
2. Grant and Steynorock, 1982
3. Kowalski and Pang, 1979
4. Pavloglou, 1987
5. Kowalski et al., 1984
6. Duen and Rosen, 1984
7. Goren et al., 1982
8. Simpson and Collins, 1980

Table 14. Comparison of stream restoration coefficients K_r (day⁻¹) determined through the use of H^+ , with values derived from predictive models (from Biline et al., 1993).

References	Santa Fe River	
	River Mile	Run 14300
O'Connor and Robbins, 1998	3.1	3.9
Breckel and Grish, 1988	4.3	4.8
Gschwendler and McFormick, 1989	4.7	3.4
Green and Sandy, 1998	1.8	1.1
Regulencia and Nakayachi, 1999	2.7	2.8
Padden and Graybe, 1971	1.3	1.6
Binnel, 1979	0.8	1.0
Bennett and Brinkman, 1972	5.4	1.4
Bennett and Brinkman, 1972	8.8	4.9
Frankhamel and Penney, 1972	1.8	1.8
Churchill et al., 1948 (I)	0.1	0.9
Churchill et al., 1948 (II)	1.1	1.4
Langbein and Burau, 1947	1.8	1.1
Green et al., 1984 (I)	5.4	1.6
Green et al., 1984 (II)	2.1	1.9

CHAPTER 1 SUMMARY AND CONCLUSIONS

Mixing

In the karstic terrain of the western Santa Fe River basin, assessing mixing parameters of the stream is made difficult by the numerous springs, seeps, seeps and boils found within the Santa Fe River. Three detailed mixing experiments were devised to address the variability in the volatile dissolved gases, natural radon-222 (^{222}Rn) and artificial sulfur hexafluoride (SF_6).

These experiments revealed that 1) sulfur hexafluoride is an efficient and useful stream tracing agent that allows for the characterization of stream parameters such as velocity, mixing (lateral, vertical and horizontal), and spring influence; 2) the injection of SF_6 into a stream with no prior knowledge of springs or seeps may also indicate the location of such features; 3) naturally occurring ^{222}Rn can also be used to interpret spring influence and mixing characteristics throughout a stream cross section; 4) concentrations of ^{222}Rn decreased with depth and appear to be dependent upon source area; 5) the overall average cross section concentrations correlate well to both the vertical and horizontal samples taken at the midpoint of the stream

and if future river water sampling should be done in an integrated fashion to account for concentration variabilities that may exist in the stream cross section, even though complete mixing is assumed in the reach of the river.

Tracing

A previously selected ground water, generic tracer, SF_6 , was introduced into O'Leary Sink, Jim's Sink and Sweetwater Lake on three different occasions in order to establish travel times through the park and detect possible points of input from ground water. The tracing experiments demonstrated that 1) the underground Santa Fe River moved through a single conduit in the top one-third of the park; 2) the river flows at a constant rate through the park and intersects sinks consecutively and continuously downstream of O'Leary Sink to the River River; 3) mathematical equations used normally to predict the rate at which surface water moves within a stream are applicable to estimate the rate at which ground water has moved through the park, supporting the idea of non-geologic flow conditions.

Flow component

The multiple application of various natural tracers revealed the location of a significant source of ground water to the system beyond Jim's Sink. In addition, it was

found that 1) the temperature data provided as much useful information as the other more complicated techniques and it was also useful in a conservative nature to estimate the relative mixing of surface and ground water; 2) temperature, geophysical, triton and oxygen isotope data show identify the distribution of and connections among ground water, surface water and wetland water; 3) because of the rapid nature that the Santa Fe River and ground water moves through C'lene State park (about 1 km/day) and the depth at which the water appears to be moving, about (20 m below land surface) the wetlands located throughout C'lene State Park do not largely contribute to the underground system of the Santa Fe River.

Discussion

Utilizing the decrease in ^{222}Rn concentrations along the two reaches, a gas transfer velocity of 27.3 h/d and a K_L value of 18.7 day^{-1} were calculated. These values are within the same order of magnitude as other streams reported.

It was determined that 1) ^{222}Rn is unacceptable as a gas exchange tracer in these reaches because of complex and incomplete mixing of ^{222}Rn enriched ground water delivered by numerous springs and seeps creating complex cross-stream and vertical concentration gradients in the river; 2) stream channel characteristics caused the rate of gas transfer, along short intervals of a few hundred meters between

sampling locations on the river, to have a high degree of variability; 3) gas exchange experiments should be completed in river length long enough to average in channel morphology as well as hydrologic characteristics; 4) since existing predictive equations to estimate gas transfer and reaeration coefficients are site specific, it is difficult to apply them in different hydrologic settings.

Computer Modeling

An attempt to develop a computer model of the study area was completed. It was determined that due to the complex hydrogeologic nature of the basin and the inability of current computer models to address specific hydrologic parameters, computer models are not suited to accurately characterize ground water and surface water conditions.

Water Sampling

The results of this research confirmed several aspects of SP_4 . Most importantly they include that 1) SP_4 is chemically and biologically inert, capable of being detected in extremely low concentrations, and is well suited for water tracing and mixing applications in karst basins; 2) in comparison to fluorescent dye tracers, such as rhodamine WT , SP_4 has the advantages of detectability at low concentrations and none of the interference problems associated with organic acids, dissolved particulates, and

equifer material that can occur with fluorescent dye: 3) SF₆ has the potential as a quantitative tracer under specific closed conditions: 4) SF₆ may also be applied to geotechnical problems such as well completion tests, and detecting upward leakage through a confining layer. The draw backs of SF₆ are that 1) construction of the analytical equipment is a snap; 2) it is a volatile tracer and is lost quickly to the atmosphere and 3) sampling SF₆ is often time consuming and labor intensive.

Forest Development in the Wilson State Park

The landscape within the western Santa Fe River Basin is a snapshot in time. The time scale of the park's evolution is many orders of magnitude slower than that of our human observation. Some landforms in the park are relatively young, such as New Stick. Others are vastly older, formed perhaps by the slow sculpturing of limestones since the early tertiary. Determining the time at which events occurred to develop the park is difficult.

Historical factors such as temperature, sea level, oceanic climate levels, rainfall and depositional environment have varied drastically since the deposition of the massive limestones that underlie the park and house the conduit system for the Santa Fe River. Ocean and surface landforms record some of the history; the difficulty is unraveling the record (White, 1994). The conduit system within the park

has NOT been explored and described in detail, and thus leaves many questions unanswered about its nature.

Based on these experiments and surface features it has been determined that Jilene Sink is the initial sinking point of the Lucha Fo River. The river travels at about 1.5 km/day, underground, in a single conduit and periodically returns to surface and then disappears at several points along its upper reach. Up to Jin's Sink there appears to be little ground water seepage into this flow. Downstream of Jin's Sink there is more ground water mixing with the Lucha Fo River and its flow becomes more diffuse. The river eventually discharges at the River Plain with a geochemical and temperature signal much more like that of ground water rather than surface water.

The age of the surface sinks may be estimated by the age of the surrounding wetlands that surround the sinks. For example, where Saw Sink opened there are now small cypress saplings, an obligate wetland species, taking root. In contrast, surrounding Jin's Sink, there are many cypress trees with eight foot diameter trunks making this sink a much older feature. Also, if the trunks of the cypress trees appear to be falling into the sink this may indicate that either the sink is widening in the trees direction or that the sink opened after the establishment of the cypress trees. Using these two ideas it may be possible to establish an age relationship among the various sinks in the park and

than a relationship between the conduit system and the wetlands found within the park. That is, the wider wetlands would indicate the older karst landforms and describe how in what direction, and at what rate the park developed.

The general abundance of sinks and karst features in the upper reach of the park versus the downstream end of the park indicates that the upper reach is more active. The reason for this higher activity in this part of the park may be due to two things. First, the upper reach has only one conduit for the Santa Fe River. If there is only one conduit for the same volume of water that flows through the lower reach of the park, it must be larger, and is therefore more likely to increment the surface causing a collapse and sink formation. Second, the nature of the water in the upper reach is that of surface water. This water is more undersaturated with respect to Ca^{++} , and is more capable to erode the underlying limestone.

Now sink has migrated to the north about in over the past two years. This process will continue as the small sinks converge into large sinks and new sinks continue to appear along the pathway of the underground Santa Fe River. The upper reach of the park will soon quickly become a surface feature for the Santa Fe River and perhaps Jim's sink will eventually appear to be the sinking point of the Santa Fe River in the future. Accompanying the development of the largest surface feature, wetlands will also coincide

lining the banks of the new portion of the river and appear much like that of the eastern part of the Santa Fe river basin.

APPENDIX B.
GAS CHROMATOGRAPHY AND THE INTERVIEW FOR SYSTEM

Gas Chromatography and the Injection Port System

Introduction

This section provides the basic instructions to operate the Shimadzu gas chromatograph (GC) equipped with an electron capture detector (ECD) for the analysis of sulfur hexafluoride. It gives a brief overview of the component parts of the system but does not go into detail about their construction, design and specific functions. This section will provide the user with a basic working knowledge of the equipment but the user should at no time attempt to "fix", or "repair" the instruments without further consultation or assistance from someone who is more capable of doing so. The equipment is expensive and extremely sensitive, therefore even the slightest wrong adjustment or operation of the system can render the system out of commission for months and require expensive repair. It is also important to read all of the instructions before attempting to run the system.

At all times should there be any type of petroleum product in the lab, even if the GC is not being used. This especially holds true for WD-40 and other aerosol products. Smoking is also strictly prohibited from the lab at any time.

Also, because of the sensitivity of this system the setup of the system may take one or more days to accomplish.

therefore if planning an experiment, make sure to start the system running at least 24 hours before analysis is to occur.

Details of the GC system

The GC system has been designed so that negative SF₆ analyses can be completed efficiently and relatively quickly. If the system is operated properly, approximately 18-20 samples can be analyzed in one 8 hour period. The analysis can detect SF₆ in concentrations as low as single parts per trillion with a precision of 14.

Equipment

There are six component parts of the entire gas chromatographic system. All parts must be in excellent working order or the analyses will not be able to be completed accurately, if at all. With reference to figure 43, the system consists of: 1) 2 (two) ultra high pure grade nitrogen tanks, 2) electric-heat gas purifier, 3) multi-port injection system, 4) gas chromatograph, 5) integrator, and 6) 3 SF₆ standard tanks.

Equipment functions

1) Nitrogen Tanks.

A) This tank acts as the source of the carrier gas for the sample of gas injected into the GC. This gas will

essentially push the sample gas through the system to be first separated and then analyzed.

B) This tank acts as the source of gas which is used to fill the headspace of the syringe which holds the other sample. Once shaken the SF_6 will diffuse into the headspace of the syringe and then be injected into the system.

2) Kinetics-test Gas Purifier.

This component removes any contaminants that may be in the carrier gas.

3) Multi-port Injection System.

This component first separates individual gas components in the sample gas and then consistently delivers equal amounts of injected sample gas to the GC for analysis.

4) Gas Chromatograph.

This component measures the amounts of individual gases found in the injected sample gas.

5) Integrator.

This component interprets the data gained from the GC and provides a printout of the relative amounts of gases found in the injected sample gas.

6) SF_6 Standards.

The standards are known concentrations of SF_6 . They are used to generate a calibration curve by which sample

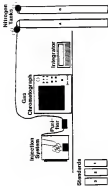


Figure 43. Gas chromatograph setup for SF_6 analysis.

data will be compared to, to obtain actual concentrations of SP_2 .

General Procedure

Before beginning to turn anything on there are several items that should be checked. Also take a minute to familiarize yourself with the individual components of the system. The items that need to be checked include:

- 1) that there is enough paper in the integrator,
- 2) that there is ink in the ink jet printer on the integrator,
- 3) that there is nitrogen, at least 100 psi in each tank,
- 4) the glass purifier. It should be black with some brown at each end. If it is totally brown it needs to be replaced,
- 5) that all equipment is plugged in properly,
- 6) that there is a desiccite tube hanging from the injection port. If it is not there one will have to be made. It consists of desiccite, glass wool and tygon tubing (Figure 14),
- 7) make sure that there is water in the beaker set next to the main-port apertures and push the tygon tubing to the bottom of the glass.

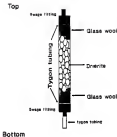


Figure 14. cross section of dinitro tube used in N_2 analysis.

Reg-line procedure

1) Turn on the H_2 tank (Fig. 43) that is connected to the GC system and adjust a flow rate to about 20 psi on the left dial of the regulator. To turn the tank on, simply turn the top tank handle counter-clockwise until it is all the way open then turn it back one-half of a turn. Watch the needles on the two dials to see if they respond. To set the pressure going out of the tanks tape the brass handle on the regulator clockwise to increase the amount of gas leaving the tanks, the left pressure gauge should be set between 10-12 psi.

2) Turn on electric-heated gas purifier.

3) Check, using "soapy", around any steel or copper connections for leaks in the system.

4) Open all capped areas on the multi-port injection system.

5) Purge the system for one hour.

6) Multi-port Injection System: Figure 45. adjust flow rates using knobs marked A and B on the multi-port system so that the flow meter on the left of the multi-port system is equal to the 5 ml bubble meter on the right side of the multi-port system. Once they have been adjusted to the same

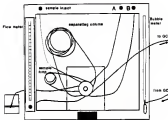


Figure 48. Multi part injection system for SF_6 analysis.

Flow rate adjust the regulator on the nitrogen tank so that they read in liters. It is important to move the switch from load to inject on the multi-port system and recheck in each location that the flow rates are the same. Note, this may take some time, be patient! The flow rate on the flow meter is determined by comparing the number to which the floating ball rises up to, to the pink sheet of paper posted on the wall behind the system. The number on the flow meter is not the flow rate, the flow rate is the number written on the pink sheet under the "flow" column. The flow rate on the bubble meter is determined by measuring the lower tube filled with soap and timing how long it takes to rise to the 1 ml mark on the types tubing. Then, by using the flow slide rule determine the flow rate through the tube.

7) OC Adjustments (the entire manual is located in the OC box located to the left of the system): Turn on the OC and set the upper temperature dial, (inject temp) to 120 by rotating the black dial to the left of the setting and set the lower dial (culture temp) to 70, using the same procedure. Always make sure that there is nitrogen going through the OC when it is running.

8) Leave entire system running for about 1 hour.

9) Recheck flow rates on both systems and adjust if needed.

10) On the front of the OC, the lower most silver knob (marked attenuation) should be set on 1, the current knob

should be set on 1.0, the bias button should be set on 1 (pressed in).

12) Integrator adjustments (a copy of the first page of the manual is found in the appendix, the entire manual is located in the dc box located to the left of the system); turn on integrator, the switch is located on the back right of the machine near the plug into the machine. First the machine will go through its own system check and give a relatively blank screen. Once it stops it will now wait for your command. Hit the LCD STARTS button, this will bring up a new display on the screen. This is the screen that you almost always want to have displayed. At the top of the screen several letters will be displayed similar to:

CM FT RLS PLOT ON ATTNX MONITOR LEVEL

The meaning of each symbol is:

CM = channel, should be set on 1

FT = file name,

PLOT = whether the system will plot automatically (AUTO), on (ON) or off (OFF)

RLS = chart speed, (in cm of paper printed per minute) it should be set on 1

ATTNX = attenuation, this is basically a filter adjustment of the signal transmitted into the integrator from the DC, set at 30.

RETIME - keeps a running time of how long the Integrator has been working.

LEVEL - the relative strength of the signal being transmitted to the Integrator.

13) Depress the ENTER button on the Integrator and then type "12" and hit the ENTER button and then hit the LOG-STATES button.

13) Now basically, if everything is going right, all major adjustments have been made.

14) Read the level on the Integrator, it should be reading quite high at first and may take several minutes to hours to days to adjust to a level of 1000 which is what you want. If it is not at 1000 or even close try adjusting the coarse adjustment knob on the OC, to get the level down to 1000. If that succeeds then switch the load/inject button on the multi-part system to the opposite position, you will notice that the level will jump probably significantly and may stay there for again minutes, hours or days? If you are lucky and the level responds quickly back to around 1000, try using the fine adjustment knob to get it to be exactly 1000 and have it remain there. If this happens, then again switch the load/inject button to the opposite position and watch the levels. It should eventually come down to 1000. AGAIN this procedure has been known to take days to reach equilibrium so do not expect any miracles and be patient.

15) If the levels do not come down within a day or so

or are certain the system has a problem and should not be used any further.

14) If the levels have equilibrated to 1000 on both the inject and load modes and the flow rates remain consistent in both inject and load modes the system is now ready for use. One final step before continuing is to hit the FT ZERO button on the Integrator. Do not hit the FT ZERO button, this will evaluate the amount of "noise" coming through the GC, the Integrator is now thinking and is averaging out the amount of noise going to the Integrator, this process takes a couple of minutes. You will know when it is finished when it prints out something like FT = 18 . The FT value should be less than 100, if not then the system is not ready to be used. This procedure should be repeated for both the load and inject modes of the multi-port system.

Now assuming all is well, i.e. levels at 1000, flow rates good, FT = <100, you can proceed with an injection. Injection of a gas sample occurs via a glass syringe, this is true for all samples but glass syringes are not used for analysis of standards.

15) Injection techniques. First make sure the Inject/load switch on the multi-port system is set on load.

16) To complete a series of standards begin with standard one, this should be marked on the top of the rack.

17) Turn on the standard tank, by turning the knob on the top of the tank. Next open the three-way-stop-cock on

the end of the standard lock hose. Now insert the end of the trap lock into the top of the drying column which should be fastened to the multi-port injection system at the location, labelled "sample inject".

20) Now slowly feed the tip of the hose and watch the glass filled with water to see if excess standard is exiting the system. This should be a slow and gradual process and not last more than a second or two. In other words do not blast gas through the system let it escape slowly. What you are doing is filling up the sample loop with a specific amount of gas and excess gas is exited to the water.

21) Wait 30 seconds, then simultaneously switch the load/inject button to inject and hit the INJECT A button on the integrator. If done correctly the printer should be going and begin plotting a relatively straight line.

22) At about 0.60 to 1.1 minutes into the injection the printer should be printing a large peak on the graph, once the peak has been completed and returns to base level hit the INJECT A button again and switch the load/inject switch back to load. At this point the integrator will begin to print out the information needed from the sample and will also temporarily store it in its memory. At this point write on the printed paper the sample number where the print out occurs.

23) If all has gone well, the levels should readjust back down to around 1800. If they do not do so immediately

let the machine run in the load mode until it does about (about 5 minutes), if it does not come back on line then obviously there is a problem in the system, most likely it is some type of contamination, and no further use of the machine is recommended.

24) Repeat steps 22-23 until the area printed out on the paper is reproducible to 2%, then move on to standard 2 and then 3 following the same procedure.

25) Injection of samples with syringes (Figure 46). The syringes should be filled with a water sample in excess of 10ml. Only the samples that are filled to greater than 10ml and have no air bubbles in them should be used, but do not throw out samples with air bubbles or ones having less than 10ml of water because they may be able to provide some qualitative data for the experiment.

26) The first step in the process is to remove the excess water in the syringes by slowly opening the three-way stop cock and pushing the water out the end up to the 10ml mark on the syringe. Next, open nitrogen tank "B" and allow some excess nitrogen flow out so that you can just barely hear it escaping. Now fill the top 10ml of the syringe with nitrogen. Carefully, insert the tip of the syringe into the tygon tubing attached to the nitrogen hose, and very slowly open the three-way stop cock to allow nitrogen to push the sample and syringe piston down ward. Be careful not to open the stop cock too quickly, you may blast the sample and



Figure 44. Glass syringe used for injecting SP_0 sample.

piston on the floor. Now allow the nitrogen to fill up the top 10ml in the syringe, so that the top of the piston should be at the 50ml mark on the syringe. Shut the stop cock and then turn off the nitrogen tank.

17) Now shake the syringe carefully but vigorously for 2 and 1/2 minutes. This procedure causes the N_2 to enter and mix in the headspace of syringe.

18) Next, make sure the LOAD/INJECT switch is set on load, insert the tip of the syringe into the drying column, open the stop cock to allow only the gases in the headspace to enter the drying column. At this time you should have some support of the bottom of the piston so that it does not drop. Now slowly and steadily push the gas and only the gas in through the system. There should be some excess gas exiting into the glass beaker to the left. Once you have pushed the gas through the system close the stop cock and take it out of the drying column. Wait 10 seconds and then as before, simultaneously hit the INJECT & button on the integrator and switch from load to inject on the multi-port injection system.

19) Follow the same procedures in steps 13 and 15.

20) Repeat with more sample syringes following steps 13-15. Consistency in filling the headspace exactly to the same level with each syringe, injecting at the same rate, shaking the syringe for the same length of time are all crucial in obtaining accurate results.

11) After 8 to 18 samples have been run, run one standard alone, and make sure it coincides with the standards run earlier. If it does not coincide run it again or run another standard. If still nothing is reproduced correctly, do not proceed any further.

12) Shut down of system. Once all of the samples have been run and standards have been run at the end of all the samples, now its time to shut the system. The system should only be shut down if no samples are going to be run over the next work shift. If more samples are scheduled to be run the next day or even within a week or so it is best to leave the system running with all equipment left on.

13) However if no samples are to be run, follow these steps strictly. First, turn off the GC and the Integrator. Allow the GC to cool for at least three hours or preferably over night. Second, remove the drying column from the sample inject port, and cap the port with a swage cap. Third, turn off the Nitrogen tank "A" and the electrical heat purifier, and allow the Nitrogen to bleed off all excess gas. Fourth, remove the heat exchanger from the bottom left side of the GC and cap the GC part with a swage cap. Fifth, get all tools, papers, and sample sheets away, and wash all bottles and syringes and place them back in their appropriate place.

Trouble-Shooting Tips

There are many things that can go wrong with this system, but fortunately if the system is set up properly and great care is taken for the system, especially where contamination is concerned it does not break down often. However when something does go wrong, another can go by trying to solve the problem.

Many "small" problems can be fixed often with little effort. A comprehensive guide to trouble shooting is provided in the GC notebook holder located to the left of the system. It is entitled "Troubleshooting Guide: How to Locate Gas Chromatography Problems and Solve Them Yourself", Guide 7000, by Supina. By looking through this guide very small problems can be located and taken care of. A copy of its front page is found in the appendix.

Take Out Procedure

The take out procedure is the technique used on the GC and separating column to recondition the column to enhance its performance. The procedure takes place in the GC oven. It is completed by following these steps:

- 1) If the GC has been running turn it off, and open the GC oven door, but continue to let the nitrogen gas flow through the system. Let the GC cool for about two hours or more.

- 2) Once it has cooled, disconnect the column from the

multi-port injection system, and cap the openings left on the multi-port system.

2) Disconnect the main nitrogen gas line from the injection board and re-attach it so that gas is flowing directly into the GC and bypassing the injection board completely.

3) Inside the oven disconnect the fitting upstream of the larger steel tubing and insert the column in this gap in flow. Reconnect the column in this area and tighten all fittings. Check for leaks using soap and correct them if needed.

4) Close the oven door and lower the flow rate of nitrogen to 15 psi, by adjusting the top handle on the nitrogen tank.

5) Set the Inject temp to 180.

6) Set the oven/column temp to 80 and let run for one hour.

7) Next set the oven/column temp to 100 and run for one hour.

8) Finally set the oven/column temp to 210 and let run for two hours.

9) Now turn off the GC and open the oven door let the system cool for at least two hours.

10) Remove the column and replace it on the injection system, reconnect the steel tubing in the oven, and

reconnect the copper tubing to its original location on the injection system.

6) After all connections have been made recheck everything on the system with soap and begin the startup procedure for running the GC system.

APPENDIX B
OF INFORMATION SYSTEMS

SP₂ Injection System

Numerous attempts were made by R. Elser and T. Elwood to efficiently design an injection system that would deliver at a consistent rate the SP₂-enriched river water to the river. The design had to be field sturdy, easy to transport, relatively inexpensive, and most importantly reproducible. The final design was reached after numerous attempts and was only slightly modified after nearly two years of continued use. The design included: A) a 700L SP₂ tank, B) a two stage regulator, C) 330 liter plastic barrel, D) a peristaltic pump, E) a 12 volt battery, F) lines of 4.5mm type tubing, and several 3 pound lead weights (Figure 47). The general theory was to aerate water with SP₂ and then inject the water into the river or sink. Previous experiments that injected the SP₂ directly into a water had problems of gas loss immediately to the atmosphere (personal communication, R. Manivickar, 1991).

In most cases the injection system would be set up and tested in the field the evening before the experiment was to take place. The general set up procedure involved first filling the 330L barrel with river water by hand dumping

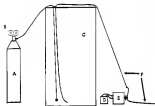


Figure 47. SF_6 field injection system used throughout all injection experiments.

five gallon buckets of river water into the top opening of the barrel. The next step would be to connect a one meter piece of tygon tubing to the copper tubing that already was fitted with a diffusion stone at its end. The end containing the diffusion stone was first threaded through a rubber stopper and then into the barrel, where it lay nearly at the bottom. The opposite end of the this piece of tygon was connected to the two stage regulator that is controlling the outflow of SP_2 to the barrel.

Next, another two meter piece of tygon tubing was threaded through the same rubber stopper and placed also at the bottom of the barrel. The opposite end of this tygon tubing was attached to a "T" fitting which opened two lines going into the peristaltic pump. On the wet line side of the peristaltic pump, two separate, appropriate length pieces of tygon tubing were then attached out into the water, and held on the bottom with lead weights. The peristaltic pump was then connected to the 12 volt battery and the system is complete for injection.

The initial phase of injection involved saturating the river water in the barrel with the SP_2 . The SP_2 would vigorously be injected into the airtight barrel for about one minute. After this, the two stage regulator would be turned down so that the back pressure on the regulator read about 2-3 psi. By continuously allowing SP_2 to enter the barrel, it assured complete saturation of the river water

throughout the injection. After time the plastic barrel was swelled with the increasing pressure so that the SF₆ had to be turned down.

Once the water was saturated, after approximately five minutes, the peristaltic pump was turned off and the water would then begin to flow from the barrel to the river. During most occasions particulate matter that had been transferred into the barrel would be seen moving through the clear tubes taking measuring that the water was actually being injected. The injection rate for the experiments was approximately two liters per minute, which allowed for at least a two hour injection.

APPENDIX C
CATION HOT-CELL PREPARATION

The cleansing process consisted at first rinsing the bottles in deionized water, second the bottles were then filled with three normal nitric acid and left standing overnight. Next the nitric acid was emptied and then the bottles were rinsed thoroughly with triple distilled water. These bottles were left to air dry, capped and then ready for sampling. Water samples were again taken at about 0.5 m where paramecia. The fifty milliliter collected sample was then packaged for transport back to the lab for analysis.

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BIOGRAPHICAL SKETCH

Richard A. Siefert was born to Gerald E. Siefert and Nancy R. Siefert on December 25, 1928 in the small, upstate town of Cobleskill, New York. He graduated from Cobleskill High School in 1946. He attended Marietta College in Marietta, Ohio, where he received his Bachelor of Science degree in Geology in 1949 while lettering and captaining the soccer team for four years. He then obtained his Masters of Science degree at Old Dominion University in Norfolk, Virginia, in the Fall of 1950. While attending Old Dominion University he worked at the University's Applied Marine Research Laboratory as a wetland investigator and hydrogeologist. In addition, he worked with The Nature Conservancy on his masters thesis in the Outer Banks of North Carolina. In the Fall of 1952 he attended the University of Florida. While attending the University of Florida he worked as a teaching assistant, research assistant, and athletic tutor. Over the last two years he has worked with consulting firms in Jacksonville, Florida, as a hydrogeologist. He was married to Hilda T. Tobey on September 21, 1958 and July 21, 1961.


I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


Douglas L. Smith, Chair
Professor of Geology


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James L. Eason
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Dean, Graduate School